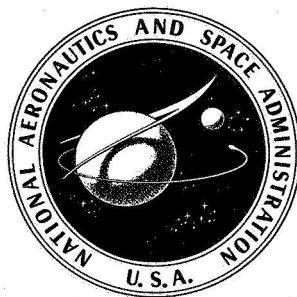# ACCELERATED TESTING
OF
SPACE BATTERIES

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ACCELERATED TESTING
OF
SPACE BATTERIES

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FOREWORD

The accelerated life test program given in this publication is believed to be the first such program for space batteries that fully satisfies empirical, statistical, and physical criteria for validity. As such, the program is believed to advance significantly the state of the art of such testing by pointing a way toward a single-test program that might ultimately be reduced to a single-sample test.

When this project (NASA Contract NAS5-11594) began, a review of the literature indicated that no generally accepted procedure was available for relating electrical changes in cells to their failure mechanisms. There seemed to be little agreement on how to set up accelerated test programs to predict performance life. However, there did seem to be general agreement about two assumptions: Cells may have a quality that tends to degrade with aging, and the rate of degradation of that quality can be accelerated by increasing stress. Starting with these assumptions, and during the subsequent development of the physical approach to accelerated testing, it was found necessary to generalize the meaning of stress to include thermal and other nonmechanical stresses. This generalization of stress was developed in such a way that the defined qualities can be degraded by the identified stresses. The usual meanings of mechanical stress, strain, and rate of strain were retained as specific illustrations of the more general meaning required for the development of the accelerated test procedures.

Persons reviewing or discussing the original work had some difficulty in accepting or seeing how to use the generalized meaning of stress, strain, and rate of strain. One difficulty with accepting the definitions is that no single book or reference can be referred to for the defense or the explanation of the physical approach recommended. The authors show that the generalized definitions of stress, strain, and rate of strain are consistent with a vast body of accepted knowledge in physics and physical chemistry. Moreover, the more general meanings make this existing knowledge relevant to the subject of accelerated life tests. Where apparent contradictions exist in the development of the physical approach (as they did in some aspects of thermal and radiant energies), similar contradictions already existed in classical physics and thermodynamics and are recognized in the literature. Therefore, the authors propose that readers assume the definitions, and the test program, to be correct until evidence can show otherwise. To assume the opposite (that is, to assume that the program is incorrect until proven correct) is to imply that a vast body

of accepted physical knowledge is perhaps incorrect or irrelevant. The authors find this implication to be untenable.

A second difficulty usually appeared when readers tried to proceed from the proposed concepts of stress, strain, and rate of strain to the actual selection of experimental conditions. Thus, a person might accept the assumption that higher stress levels will increase the degradation rate of electrical quality, and he might accept the definitions given herein for electrical quality, stress, rate of strain, and so forth; yet that person may still not be certain how the test program should be set up. This uncertainty arises because no single test is recommended herein. Instead, the recommended program requires a fore-knowledge about intended-use conditions and about failure mechanisms. It may be that neither intended-use conditions nor failure mechanisms are known; but whether they are known or not, the naming of one predominant stress, the selection of a maximum stress level, and the identification of independent variables to create the required stress levels all appear to require new kinds of decisions for electrochemists. Naturally, such new and complex considerations create uncertainty about how to proceed. It is precisely because of this uncertainty that the authors recommend a test program to blend empirical, statistical, and physical approaches with whatever knowledge is available about intended-use conditions and the anticipated failure mechanisms. If such knowledge does not exist, the authors recommend a fractional factorial design experiment whose size is limited only by costs. On the other hand, if the knowledge about spacecraft cells is complete, the authors recommend a single test with a single sample. The test program described herein requires the use of whatever knowledge can be obtained by those setting up the test conditions. The plan then provides physical examinations, statistical treatments of the data, and empirical observations of the cells and the data to support or to correct the starting assumptions. The plan is expected to be used with more certainty and is expected to become simplified when accepted test results justify such attitudes.

on management of large space battery evaluation programs; W. J. Shobe of NAD Crane served as a consultant on statistical modeling; and John Lannan of NAD Crane served as a consultant on failure prediction and analysis.

CONTENTS

SYMBOLS

a	area
c	charge current; concentration; ampere-hour capacity; number of cells required for initial tear-down analysis
C'	heat capacity
D	charge duration; diffusion constant
E	electric potential
emf	electromotive force
F	force
f	frequency; function
G	acceleration of gravity
g'	specific mass in grams per ampere-hour
H	magnetic potential
h	height; Planck's constant
I	current; intensity factor
k_n	coefficient of proportionality for equation n
L	illumination; stress level
l	length
M	manufacturer; matrix
m	mass
N	total number of cells required
n	hourly rate at which a cell is charged or discharged; number of observations
O	osmotic pressure
P	percentage of cells exhibiting a given failure characteristic; mechanical pressure; number of independent test programs
p	sound pressure
Q	electric charge
Q_0	average initial electrical quality
Q_f	preset quality level associated with failure
Q_I	quality as a function of an intensity gradient
Q_p	pressure quality
Q_s	quality as a function of stress
Q_t	temperature quality
Q_v	voltage quality
Q_π	quality of some parameter π

$\overline{Q}$ average quality

$\hat{Q}$ predicted quality

R constant rate of degradation of quality; number of identical cells at a given stress level

r radius

S number of stresses

SSD sum of squared deviations

s stress

T temperature

T' torque

t time

t_{ij} parametric prediction time for which i is the stress level and j is the index of the predicted time

t' time of charge or discharge

$t*$ fixed time in early-life measurements

V voltage; volume

V_m molar volume

v velocity

x length

α magnetic pole

γ surface tension

η viscosity

λ acceleration factor

π parameter

τ_n time constant in equation n

ϕ angular displacement

1 ACCELERATED LIFE TESTS

A review of the literature pertaining to accelerated life testing of secondary spacecraft batteries reveals that little is actually known of the processes associated with the rates of degradation or of the phenomenological laws associated with degradation processes. In the past, an operational life test was sometimes called an accelerated test if the operating conditions gave a shorter cycle life. When, by trial and error usually, those operating conditions that increased the rate of degradation were found, extrapolations to normal conditions were made under the assumption that the degradation processes did not change. Until quite recently, this approach predominated in many laboratories. A reevaluation of the whole problem of accelerated testing of spacecraft batteries is now in progress. This reevaluation has resulted from the need for accelerated tests that can be interpreted phenomenologically and unambiguously and from recent advances in the theory of accelerated-testing techniques developed for nonelectrochemical energy storage devices.

This section summarizes previous work in the field of electrochemical energy storage devices, indicates the inadequacies of this work, and includes a review of general theories of accelerated testing of nonelectrochemical devices. A review of the use of data reduction and analysis as a predictive tool in accelerated testing concludes the section.

Several key terms are defined and used in the following paragraphs. The definitions are taken from a report on failure mechanisms and accelerated life testing prepared for the U.S. Air Force (Reference 1).

A secondary cell is assumed to possess a certain quality that is measurable in quantitative terms. It is further assumed that over a sufficient time, the quality of a cell will degrade. A widely used description of battery quality is the guaranteed life. That is, a battery with a 3-year guarantee is generally taken to have a higher initial quality than a battery with a 2-year guarantee. Such a general description of quality, however, is not suitable for accelerated life tests. For the description or definition to be suitable, it must be conceptually possible to measure the quality of a battery at any time and practically possible to measure the quality at least within the charge or discharge cycles. Such in-cycle measurements can be used to observe the quality from one cycle to another. The changes of the in-cycle quality over a period of many cycles can be used to determine the time rate or cycle rate of degradation of quality. It

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has been suggested that at least three definitions of quality based upon the above considerations may be necessary to describe the characteristics of a secondary cell (Reference 1). These three qualities are voltage quality Q_v, temperature quality Q_t, and pressure quality Q_p; they were suggested because changes in voltage, temperature, and pressure are observed in each cycle during cell operation.

For the purposes of this discussion, a high-quality battery is defined as a battery that exhibits small changes in measurable parameters during closed-circuit operation within a cycle that begins with the closing of the circuit.

Mathematically, quality may be expressed as

$$Q_\pi = \frac{1}{\Delta \pi n} , \tag{1}$$

where π is the voltage, temperature, or pressure parameter chosen for measurement and n is the hourly rate at which the cell is charged or discharged. With n included in the definition of quality, the rate of charge or discharge is related to battery size.

One consequence of this definition of quality is that those cells that allow the highest C/n rates of charge or discharge will have the highest quality. Therefore, silver-zinc cells will have a higher initial voltage quality than nickel-cadmium cells. This follows because, for a given change in voltage ΔV, the silver-zinc cells will discharge at a smaller hourly rate. However, the number of cycles required for a given amount of degradation of quality depends also on the cycle rate of change of quality and not only on the initial quality.

At any given time, the operation of a secondary cell is assumed to be associated with a certain level of stress. A report by McCallum et al. (Reference 1) states that stress for a secondary cell is always expressible as an intensity factor of some form of energy. The report indicates how stresses can be distinguished from strains (expressed as a capacity factor) and concludes that there are four principal stresses associated with the operation of a battery: temperature, voltage, gas pressure (as a mechanical force), and mechanical forces introduced by cell construction (e.g., by the use of retaining plates or electrode structures).

Higher rates of degradation are assumed to occur at higher levels of stress. In an acceptable accelerated life test procedure, the mechanisms of aging, associated with the time rate of degradation of quality, must be the same at the high level and normal level of stress. Also, failures should occur because of the gradual degradation of quality and not by some instantaneous (catastrophic) means. In the latter case, interpretation and extrapolation of the test results may be very difficult, if not impossible.

Although various approaches to accelerated life testing are possible, there are several assumptions common to most of these approaches:

(1) The quality of a component varies over time; after sufficient time, the quality degrades.

(2) The rate of degradation of quality depends on the level of stress experienced by the cell during its operating life.

(3) Higher degradation rates occur at higher stress levels.

(4) The degradation of quality will eventually lead to failure.

Accelerated tests are performed to establish acceleration factors in a short period of time that permit degradation rates at low levels of stress to be predicted by using degradation rates obtained at high levels of stress. In simple cases, the acceleration factor is equal to the ratio of the rate of degradation at the high stress to the rate of degradation at normal stress. Accordingly, the larger the acceleration factor the more efficient and desirable the accelerated life test, provided that the dominant failure mechanism is the same for both the accelerated and normal operating conditions.

ACCELERATED TESTING OF ELECTROCHEMICAL ENERGY CONVERSION DEVICES

The main source of references concerning the accelerated life testing of spacecraft batteries is the Battery Workshop Proceedings (Reference 2); this workshop was sponsored by NASA, and more than half of the speakers presented papers related to accelerated testing of batteries. Three generalities may be extracted from the papers:

(1) Any accelerated life test should only hasten normal failure processes; that is, the test should not change the primary causes of failure.

(2) An accelerated life test should be related to service conditions to facilitate interpretation and application of the results.

(3) Methods for accelerating operational life tests are uncertain because of a lack of knowledge of the principles involved in testing such complex devices as spacecraft batteries and also because of a lack of knowledge of the aging mechanisms and their physics and chemistry.

In many life tests, several variables are often associated with relatively short cycle life. These variables include increases in temperature, load, or current; depth of discharge; and rate of charge or discharge. Higher levels of these variables are usually identified with the higher levels of stress discussed earlier. Because increasingly higher levels of these variables appear to shorten cell life with no apparent change in failure determinants and because some interpolation and extrapolation of the data to other levels of stress are possible, the tests are often described as being accelerated life tests. For these reasons, it is convenient to discuss the literature in terms of those variables that are found to affect the cycle life.

Temperature increases sometimes lead to shortened cycle life and constitute the most commonly used stress. Some reported tests have been analyzed according to an Arrhenius-type model (Reference 3). This represents a certain degree of sophistication over other methods of analysis (Reference 4).

In a research project concerned with the development of improved, sealed nickel-cadmium batteries (Reference 4), Gulton Industries has reported on operational life tests performed at elevated temperatures. It is reported that the "accelerated elevated temperature cycling" of three-plate cells, made with candidate separator materials, appears to be a very informative test. Where shorts appear in the elevated temperature test, the nature of the separator defects appears to be the same as those encountered in the failure analysis of cells failing under normal operational conditions. Thus, it may be assumed that separators showing a small probability of failure on the accelerated life test would also show a small probability of failure during continuous charge/discharge cycling.

Willihnganz, in a paper at the NASA Battery Workshop (Reference 5), emphasized some of the generalities given above. Although he describes the accelerated testing of lead-acid automobile and telephone batteries, his remarks apply to any accelerated life test procedure and are paraphrased as follows: First, in setting up life tests it is desirable to have prior knowledge of why and how the battery will fail; any accelerated test must, then, cause similar batteries to fail by the same mechanism. Second, if the service conditions to which the batteries are to be subjected are changed, the tests must be altered accordingly. Third, the results of accelerated tests must be compared with the results of field tests under normal levels of stress to insure that the failure modes and determinants are the same.

A linear relationship between the logarithm of cycle life and the reciprocal of absolute temperature is qualitatively described by Willihnganz in his paper on the testing of telephone batteries (Reference 6); extrapolation to a temperature of 298 K (25° C) to predict life is said to be possible. Because the normal life of telephone batteries is about 20 years, such an extrapolation to normal temperatures is desirable.

Biddick, at the NASA Battery Workshop (Reference 7), reported upon work at Bell Telephone Laboratories. Studies were made of the growth of the positive plates in lead-acid telephone batteries as a function of increasing ambient temperature. Over a test period of about 20 years (Reference 8), and in later studies (Reference 6), the rate of growth of the positive plate was found to nearly double for each 10-K (10-C°) incremental increase in temperature at a given overpotential of the electrode. At about 355 K (82° C), the growth rate was 60 times that at room temperature (Reference 5). Thus, 20 years of growth could be obtained in 120 days. Furthermore, the failure mode and failure determinants appeared to be the same for the normal operational life test and accelerated test run at an overpotential of 75 mV. This seems to be an ideal test for lead-acid, stationary, emergency batteries. An acceleration factor of 60 is very large indeed. It appears that no other sources have reported validated acceleration factors of this magnitude.

Screening tests of prototype silver-cadmium cells at elevated temperature have been described by Scott (Reference 9). The results were limited, and the

author declined to make any extrapolation or interpolations based on only two measurements [room temperature and 333 K (60° C)]. It may be inferred that the 333-K (60° C) temperature was chosen to reduce the test time, although this was not elaborated.

The effects of temperature increases on chosen variables were described semiquantitatively by Bowers in a paper on the nondestructive testing of silver-zinc cells (Reference 10). Bowers stored the charged batteries for 3, 6, and 12 months at ambient temperatures of about 294, 316, 323, and 333 K (21°, 43°, 50°, and 60° C). The ampere-hour capacity was measured and also calculated from the silver and silver oxide content. At 294 K (21° C), there was little change in chemical composition or ampere-hour capacity during the 12-month period; similar observations were made during the tests at 316 K (43° C). At 323 K (50° C), chemical changes in the silver electrode were observed because of silver (II) oxide decomposition. Also at 323 K (50° C), there was a drop in ampere-hour capacity from about 105 to about 95 after 1 month of storage. At 333 K (60° C), after 1 month of storage, the loss in measured capacity increased to approximately 30 percent, and after 6 months of storage there was practically no silver (II) oxide remaining in the silver electrodes.

If the mechanism for silver (II) oxide decomposition and the loss in measured capacity can be shown to be the same over this temperature range, there exists the possibility of designing an accelerated life test based on these observations. However, Bowers pointed out that, at about 323 K (50° C) or above, physical degradation of the case material also occurred. This fact would impose an upper limit on the range of selected temperatures.

Chreitzberg (Reference 3) also performed experiments similar to those of Bowers and measured the loss in ampere-hour capacity of silver-zinc cells stored at temperatures in the range of approximately 273 through 323 K (0° through 50° C). Plots of the logarithm of the measured capacity versus storage time at each temperature level were essentially linear, although there was not much separation between the curves for the 273- and 288-K (0°- and 15°-C) data. For cells stored between about 288 and 323 K (15° and 50° C), the results obeyed an Arrhenius-type relationship. That is, when a straight line plot was obtained, the slopes of the linear plots of log capacity versus time were plotted against the reciprocal at absolute temperature. Chreitzberg stated that there was some theoretical justification for the slope of log capacity versus time to be proportional to the rate constant for the reaction associated with the capacity loss. The slopes of the Arrhenius-type plots were found to be in the range 20.5 to 22.5 kcal/mole. From this, Chreitzberg concluded that there was probably only one overall activation energy for the reactions that occurred in silver-zinc cells of differing construction.

Chreitzberg's analysis of his experiments in terms of a physical model based on an Arrhenius-type model suggested that a mathematical and phenomenological model for the accelerated life testing of spacecraft batteries might be

possible. Chreitzberg concluded that the cycle life of secondary cells could be estimated from such storage tests with acceleration factors that would probably lie in the range of 2 to 3.

In contrast to this optimistic statement, the discussion of storage temperature used as a level of stress should be appended by the following statements by Sulkes (Reference 2) related to charge/discharge cycling at elevated temperatures:

> When cycling is done at an elevated temperature in an attempt to speed testing, the resultant cycle life may be increased if poor charge acceptance is the cause of failure, or decreased if the failure mechanism is silver attack on the separator. Increasing the number of cycles per day to speed testing may shift the failure mechanism from shorting, to capacity loss caused by negative shape change. It is clear, therefore, that in most cases the testing of experimental silver-zinc cells cannot be accelerated . . . .

As a reply to this pessimistic view of accelerated testing, it appears that the following argument needs to be considered. Consider a battery operated under a reference (normal) set of conditions. Under these normal conditions, it is assumed that although several failure mechanisms occur simultaneously, only one of these mechanisms dominates. That is, failure will result from exactly one of these competing, underlying failure mechanisms, and the dominant mechanism is completely determined by the operating conditions. Now consider that the operating conditions are changed to achieve an accelerated test. If the change is sufficiently small, it is asserted that the dominant relation will not be changed; therefore, failure will occur for the same reason as that associated with normal operating conditions. If the dominant relation were changed for any arbitrarily small change from the normal operating conditions, it would suggest that the two competing failure mechanisms change relative importance exactly at the operating conditions. Because this is unlikely, it follows, in general, that some change can be made to achieve an accelerated test. It is true that the change may be so small that the reduction in test time may not be impressive; however, the argument is intended to show that *some* acceleration is obtainable. The real question is *how much* acceleration is possible without changing the dominant failure mechanism.

The rate of discharge or charge is mentioned several times in the literature as one possible variable for controlling an accelerated life test. Biddick, in tests on nickel-cadmium cells in which the rate of charge/discharge cycling was varied (Reference 7), found that changes in the observed ampere-hour capacity with cells cycled eight times a day differed little from cells cycled two times a day. Moreover, in both cases a gradual loss in capacity of the negative plates occurred. Biddick thus obtained an acceleration factor of 4 and concluded that the rate of degradation was a function of the number of cycles, not time, in these experiments.

This latter conclusion was also partially confirmed by Scott's work with nickel-cadmium cells (Reference 9). Scott concluded that the rate of

degradation is proportional to the number of cycles, provided that the rate of charge and discharge does not exceed the capacity rating of the cells. With silver-cadmium cells, high-rate cycling using $C/2.5$ currents also caused a decrease in the measured capacity. However, because of decreasing charging efficiency at this rate of cycling, the voltage-time characteristics also changed because the upper discharge plateau became nonexistent. Although physical interpretation of the results was thus impeded, the method of increasing the number of cycles per unit of time was found more satisfactory than the method of increasing the actual rates of charge and discharge.

Recent work by the General Electric Company on a reduced-gravity battery test program for silver-zinc cells has described a preliminary accelerated life test using rapid cycling with selected depths of discharge as the accelerating stress (Reference 11). The test included preliminary conditioning of the cell, followed by five consecutive 60/30-min charge/discharge cycles to 35-percent depth of discharge. Transient capacity and cell voltage measurements were made during the 90-min cycles; polarization measurements and discharge-capacity measurements were made before and after each cycle. However, none of the measurements indicated that a desirable rate of degradation of quality could be obtained when the depth of discharge was limited to 35 percent. It was, therefore, recommended that the depth of discharge be increased for future studies.

Depth of discharge has been mentioned elsewhere (Reference 2) as an accelerating stress, but a successful accelerated life test utilizing this parameter has not yet been designed. Also, Belove has suggested that the amount and rate of overcharge should be considered in an accelerated test because overcharge probably represents the greatest proportion of actual battery conditioning on a spacecraft (Reference 12).

Increases in battery load (Reference 2) or current (Reference 7), or physical intervention, such as removal of all free electrolyte (Reference 9), have been investigated as possible stresses for accelerating the rate of degradation of spacecraft batteries. However, actual accelerated tests based on these methods have not been reported.

ACCELERATED TESTING OF NONELECTROCHEMICAL DEVICES

A wide variety of life tests have been performed on components other than batteries. The areas of electronic reliability and mechanical fatigue contain many representative examples of serious attempts to obtain valid accelerated life tests. In electronics, accelerated tests have been carried out for certain types of resistors, capacitors, transistors, and integrated circuits. A large amount of the fatigue testing of mechanical components is directed toward the determination of stress levels at which the life of the component can be expected to exceed a specified design life. (The bibliography contains references to some of these efforts in electronics and mechanical fatigue.)

Although many disciplines are confronted with the problem of predicting life in a short period, it appears that an accepted general approach to accelerated life testing has not evolved. Most tests are so specialized that little information is directly applicable to other components. Consequently, references to such tests are of uncertain value to investigators in other areas.

Minimal Requirements for Accelerated Tests

Many laboratory tests are not performed for the purpose of predicting the life of a component; nevertheless, the data obtained from these tests are often relevant to making such predictions, and when this is the case, the tests may be loosely labeled as accelerated tests. In stricter terms, such tests cannot be called accelerated tests unless the following minimal requirements are fulfilled:

(1) The test conditions should involve several levels of stress that are higher than a normal stress level.

(2) Measurements of quality should be taken at successive times at each level of stress.

(3) The resulting measurements should be analyzed to determine the time rate of degradation of quality as a function of stress level; these results should be extrapolated to obtain an estimate of life at the normal stress level.

Further requirements on accelerated tests are usually imposed in an attempt to insure that the mechanism of failure has not changed at the higher stress levels. The actual methods of data analysis vary widely depending on whether an empirical, statistical, or physical approach is used (Reference 1).

Common Deficiencies of Accelerated Tests

A survey of the literature shows that several common deficiencies are often found in accelerated tests. First, it appears that too little effort is put into the task of obtaining suitable definitions of stress, quality, and failure. Such definitions must relate quantities that are both measurable in the laboratory and meaningful in the context of possible physical mechanisms associated with the operation of the component. It is often assumed that variables that describe the operating characteristics of the device are the same variables as those needed to describe how long the device will last. It is conceptually possible that those variables that indicate the quality of the device may have nothing to do with the prediction of how long that quality will be maintained. It appears that in the design of accelerated tests, much more attention should be given to the basic definitions and their associated laboratory measurements.

A second common deficiency consists of the failure to measure variables that can yield degradation rates as a function of stress level. High precision is required in the measuring techniques in order to detect and measure small degradation rates.

A third common deficiency in accelerated tests results from the use of only one high level of stress instead of a set of increasingly higher stress levels. Even if the relevant variables are measured with sufficient precision to yield the degradation rate at a single high level of stress, there is no suitable method of extrapolating this rate to obtain the predicted degradation rate at the normal stress level. At least two different high levels of stress are required to permit a straight-line extrapolation to a normal stress level; more than two levels are required to obtain evidence regarding possible changes in the failure mechanism.

Mathematical and Statistical Theories Related to Accelerated Testing

A component may be subjected to higher than normal stresses in several ways. In the constant stress approach, the component is subjected to a single level of stress, and this level of stress is maintained for the life of the component. In the step-stress approach, the component is subjected to a sequence of incrementally increased stress levels; that is, after the initial constant stress level is maintained for a specific interval, a higher level of stress is imposed for an additional interval, and the process is repeated until the component fails. In the continuously increasing stress approach, stress on the component is gradually increased until the component fails.

Special methods of data analysis have been developed for these different approaches; several references pertaining to these methods are included in the bibliography. It should be noted that nearly all of the statistical literature in the area of reliability is relevant to the analysis of accelerated test data. In general, reliability problems are concerned with the prediction of life; accelerated tests simply augment the reliability problem by requiring that the prediction be valid at a normal stress condition for which no test data were taken.

DATA ACQUISITION AND ANALYSIS

A review of the literature indicates that previous battery test programs have used rather rigid test designs. Primarily, the data records have served to monitor the functioning of equipment and to identify battery and cell histories. Computers have served mostly to retrieve specific information and to tabulate results. The data have not served as a feedback to improve the test design. If the physical mechanisms and their laws were well defined, there would be little need to provide a data feedback to the design. However, in the case of accelerated tests, all available information should be used to shorten the test time.

Two basic methods are available to provide a shorter test time. One method is based on increasing the rate of the aging process; the other method consists of obtaining more information from the test data so that cell life can be predicted from early life measurements. To accomplish the latter, a more

flexible approach to data acquisition and analysis must be taken. The data-processing capability of a computer permits a search for patterns to relate key parameters to dependent variables and to detect important deterministic and probabilistic associations within the data to determine behavior cycles. In general, empirical methods are best suited for initial data processing. Empirical methods—in contrast to the statistical or physical approaches to accelerated testing—are not based on an assumption of any prior structure in the data. Instead, the empirical approach searches for objective properties of the data. Once identified, these properties are available for the interpretation and exploitation of the statistical and physical approaches. These objective properties of the data structures and some of the empirical techniques used to identify them are described in the following paragraphs.

Empirical Techniques and Data Structure

The general structure of a set of measurements may possess some or all of the following features:

(1) A frequency distribution of measured values over time
(2) An association among measured values
(3) A repetitive cycle, or period, among measured values
(4) A functional dependence among measured values

These general features, whose presence can be quickly detected on a modern computer, provide information on patterns among the measurements. The computational effort required in these tasks virtually exceeds man's capability; but once detected, the observed patterns, in turn, can be further analyzed for both physical and statistical significance to allow development of quantitative models capable of predicting life.

The field of cryptanalysis appears to offer an existing discipline with methods and procedures for identifying important features of data structure. This results from the fact that much code-cracking work is not done on languages but on numerical information. The cryptanalytical approach includes computerized tools to detect data structure and to eliminate a prodigious amount of human effort.

There are many methods in cryptanalysis for extracting the structure of data. A review of the field suggests that four of these methods are directly related to the four objective features listed above. These four methods may be described in general terms as follows:

(1) *Distribution features.* The frequency of occurrence of the voltage measurements for a given point in a cycle may be obtained by classifying the measurements into intervals. The resulting frequency distribution can be used to regroup adjacent class intervals and thereby determine a more appropriate precision. A similar argument holds for each measured variable. If all data measurements (variables and levels

of variables) are coded by letters and the resulting codes are analyzed by a polygram frequency distribution program, a distinct pattern would be obtained for the measurements. For a nonaging component in a constant environment, this pattern would be invariant over time. If aging occurs, the patterns will change, and one can begin to establish a basis for the extrapolation of changes and possibly predict the life of the component. An examination of the patterns may also indicate whether the measurements should be taken more or less frequently. This polygram distribution technique is a conventional method in cryptanalysis.

(2) *Association features.* The interdependence of variables upon each other is an important data structure in accelerated testing. Consequently, a method is needed in which the frequency of occurrence of those combinations of variables that occur most often under certain environmental conditions can be determined. Where the number of possible combinations of measured variables is large, a computer is required to make such an analysis; with relatively few variables, the polygram technique may suffice. With a large number of variables, a more powerful technique, such as the index of coincidences (Reference 13), must be used together with proper information encoding.

(3) *Periodic features.* As the components age, periodic changes in the patterns can furnish a valuable clue for an analysis based on a more refined statistical or physical method. The Kasiski method is one technique for determining periodic structure (Reference 14). This method essentially counts the interval between the polygram repeats. From the frequency tabulation of the number variables, the period of the phenomena is determined. It would appear that proper interpretation of periodic behavior would permit the development of a predictive process early in the life of the component.

(4) *Functional dependence.* The search for more complex relations among the variables can be pursued with a number of tools. Some of these tools are associated with both statistical methods and cryptanalysis and include the use of Bayes' theorem and the Automatic Interaction Detection (AID) computer program. Bayes' theorem is based on the use of probabilistic relations; the AID program expresses the data structure in the form of a "tree."

In summary, a review of cryptanalytic methods suggests that methods exist to identify the four types of structures described above. It appears that the use of these methods concurrently with the generation of data would permit useful feedback to the experimental design. This procedure would greatly improve the efficiency of data taking. Moreover, early detection of patterns and changes in these patterns would permit the early application of statistical and physical methods to obtain predictions of component life.

For example, cryptanalytical techniques have been used to analyze some of the data generated by the Quality Evaluation Laboratory (QEL) at the Naval Ammunition Depot, Crane, Indiana, testing programs. Indications extracted from the data (charge/discharge voltage measurements, primarily) were applicable in predicting life expectancy of the cells on test after about 1 percent of their useful life had been consumed. The computer programs used generated first-difference voltage histograms that established the slopes of the charge/discharge curves between the monitoring points, superimposed charge/ discharge curves, and provided frequency counts over set thresholds.

The first set of data indicated which cells showed the greatest voltage changes per time increment chosen. There appeared to be good correlation between cells that failed and those that showed the greatest voltage changes. The second set of data indicated which cells showed deviations in electrical performance from the average performance exhibited. Once again, there was good correlation between cell failure and abnormal electrical characteristics. The third set of data gave the frequency of the excursions of the cell voltage outside limits chosen from observed normal cell performance characteristics. The greater the frequency of excursions outside the limits, the more likely a cell was to fail.

2 EXISTING TEST METHODS

Tests currently applied to spacecraft cells and batteries are predominantly oriented toward determining performance capabilities of existing battery designs and evaluating proposed battery designs. Most of these tests are life-cycle tests that are often performed until failure occurs. A subsequent failure analysis is made to determine why the cells failed. In some instances, this procedure enables corrective measures to be made.

Because of the central role of the life-cycle test, attention shall be focused on the design of these tests, including environmental controls, measurements taken, and attempts to modify these tests so that accelerated life tests are obtained. Modifications of life-cycle tests, such as increasing suspected operational stresses, comprise most of the accelerated tests reported on electrochemical devices. Adequate reviews of the principles and philosophies involved in accelerated testing of electrochemical devices have not been found.

OPERATIONAL LIFE TESTS

Operational life tests are usually classed under such terms as life-cycle tests, cycle-life tests, or cycling tests for secondary batteries. These terms are intended to imply that the batteries are subjected to a specified, repetitive charge/discharge regime. Usually, the charge/discharge regimes are arranged to simulate actual operational requirements so that the results may be applied in practice. Four programs associated with operational life tests are described below to illustrate the nature of the tests and the various degrees of sophistication.

Inland Testing Laboratories

Inland Testing Laboratories of the Cook Electric Company has performed battery evaluation programs for both NASA (Contract NAS5-1048) and the U.S. Air Force (Contracts AF 33(616)-7529, AF 33(657)-8450, and AF 33(615)-1580).

The NASA program consisted of subjecting 100 3.5-A-hr and fifty 6.0-A-hr nickel-cadmium cells to a series of qualification and acceptance tests followed by life tests and subsequent posttest analyses.

The qualification and acceptance tests included visual and mechanical inspection, capacity determinations, electrical leakage checks, overcharge capability, and internal resistance measurement. Also included were electrolyte leakage, vibration, shock, and acceleration tests. However, not all of these tests were applied to all cells.

Having satisfied the necessary qualification and acceptance requirements, the cells were separated into 10-cell groups and were subjected to an operational life test having the following characteristics:

(1) Charge time: 60 min
(2) Discharge time: 40 min
(3) One cycle: 100 min
(4) Ambient temperature: 263, 298, and 323 K (-10°, 25°, and 50° C)
(5) Depth of discharge: 10, 25, and 40 percent

The life-test-cycle regime was operated continuously until one-half the cells in each 10-cell group displayed terminal voltages below 1.0 V during the discharge portion of the cycle. The total number of cycles successfully completed by each cell was recorded.

All failed cells were subjected to visual inspection, dimensional checks, and capacity and electrical leakage (open-circuit stand) checks. For each cell, the data obtained before and after the test were compared to ascertain the magnitude of any changes. However, no additional tests were performed.

The U.S. Air Force Aero-Propulsion Laboratory contracts pertained to an evaluation of a wider range of secondary cells and batteries. Contract AF 33(616)-7529, for example, involved the evaluation of the operational life of one hundred ninety-two 25-A-hr silver-zinc cells, one hundred ninety-two 20-A-hr silver-cadmium cells, one hundred fifty 20-A-hr nickel-cadmium cells, and two hundred forty 12-A-hr nickel-cadmium cells. Most nickel-cadmium cell groups consisted of 10 cells, whereas the silver-zinc and silver-cadmium cell groups consisted of eight cells. Typical operational parameters for nickel-cadmium cells were as follows:

(1) Charge time: 55 min
(2) Discharge time: 35 min
(3) One cycle: 90 min
(4) Ambient temperature: 263, 278, 298, and 323 K (-10°, 5°, 25°, and 50° C)
(5) Depth of discharge: 25, 50, and 75 percent

Typical operational parameters for silver-zinc and silver-cadmium cells were as follows:

(1) Charge time: 85 min (or 22.8 hr)
(2) Discharge time: 35 min (or 1.2 hr)
(3) One cycle: 120 min (or 24 hr)

(4) Ambient temperature: 263, 278, 298, and 323 K ($-10°, 5°, 25°,$ and
    $50°$ C)

(5) Depth of discharge: 25, 50, and 75 percent

All discharges were made at a constant current; all charges were made at a constant current to a preset voltage limit, after which the group was charged at constant voltage. The cell groups were cycled continuously (24 hours a day, 7 days a week), and each group was controlled by its own charge/discharge cycling apparatus. (The cycle timer and counter were common for each test regime.) The charge/discharge rates were determined from the manufacturer's rated ampere-hour capacity C. Capacity checks were made on samples of each type of cell to verify these rates.

During the life tests, the cell voltages, group voltages, temperatures, and group currents were monitored. Most of the data for group voltages and currents were obtained on recorder chart paper; very little information about individual cells was permanently recorded. For this reason, retrospective analysis of the evaluation is difficult in terms of individual cell behavior.

Under Contract AF 33(616)-7529, the cell-failure criterion was the inability of a cell to deliver the required discharge current for the full time of the discharge period without the voltage falling below a preset limit. This limit was selected according to the cell type and test condition. This was done because of the differences in electrical characteristics of the cells and the effects of depth of discharge and temperature on those electrical characteristics. If a cell failed or showed some other defect that could lead to damage of other cells, the cell was removed and the group cycle parameters were reset in order to maintain the original test conditions. Group failure was said to have occurred when one-half or more of the individual cells in each group had failed.

After the operational (cycling) tests were completed, comprehensive failure analyses of selected samples of the failed cells were performed by the respective cell manufacturers. The purpose of these analyses was to determine the causes of the failures and to determine precursors associated with these causes. This procedure was used so that cell-failure mechanisms would be better understood and so that manufacturers could take steps, when possible, to avoid these failures. The failure analysis procedures, and the documentation arising from them under this particular evaluation, represent an improvement over the NASA program previously described. However, the results of this program received limited distribution and appear to have had little impact on other battery users and manufacturers.

The objectives and applications of Contract AF 33(657)-8450 were similar to Contract AF 33(616)-7529. The evaluation program was concerned with the operational life and resulting failure analysis of a large number of cells. These included two types of 25-A-hr silver-zinc cells; one type each of 15- and 20-A-hr silver-cadmium cells, and one type of 20-A-hr nickel-cadmium cell.

Test parameters, test equipment, and data collection procedures for this program were essentially the same as those described for Contract AF 33(616)-7529. Again, it appears that the dissemination of the results was limited.

Contract AF 33(615)-1580 was terminated before completion of the proposed program. As a result, little useful information was reported under this contract.

None of the foregoing battery evaluation programs were specifically designed to accelerate the aging of cells or groups of cells. Instead, the operational tests were designed to provide a broad base of data related to the operating characteristics of the cells over a range of anticipated uses and environments. In a sense, this was not achieved, because the collection of data was often poorly organized: For example, hindsight shows that more individual cell data would have been useful.

The fact that the tests were not designed to be accelerated tests does not mean that the selection of the variables did not cause aging to occur more rapidly under certain test conditions. For example, it could be postulated that the tests at 323 K (50° C) and 75-percent depth of discharge were more stressful than those tests at 278 K (5° C) and 25-percent depth of discharge. If aging occurred more rapidly under the more stressful conditions, accelerated test data were obtained. The lack of individual cell data, however, would appear to prevent a reanalysis of the observed results (cycle life) to obtain evidence as to whether the failure mechanisms were the same at the more stressful condition and, if so, to obtain an estimate of the acceleration factor.

Quality Evaluation Laboratories

Several battery evaluation programs were performed by QEL. Most of this effort is being done under NASA Contract W11, 252B. The program began in 1963 with the objective of gathering specific information concerning the performance characteristics and limitations of secondary cells under various electrical and environmental operating conditions. As a result of the program, it is intended that cell weaknesses, including the causes of failure of present designs, will be identified so that appropriate modifications can be made in future designs. Also, the large volume of data collected is intended to serve as reference material for power-system designers and users.

The original program began with 660 sealed, nickel-cadmium cells from four manufacturers and in seven capacity groups ranging from 3.0 to 20 A-hr. The operational parameters were as follows:

(1) Charge time: 1, 2.5, and 23 hr
(2) Discharge time: 0.5, 0.5, and 1 hr
(3) One cycle: 1.5, 3, and 24 hr
(4) Ambient temperature: 273, 298, and 323/313 K (0°, 25°, and 50°/40° C)
(5) Depth of discharge: 15, 25, and 40 percent

The cells cycled at 323 K (50° C) were found to have very short lives; consequently, the temperature was lowered to 313 K (40° C) for subsequent tests in order to obtain a greater volume of data. Not all combinations of the above parameters were used. Table 1 shows the combinations used, with the respective charge voltage limit and amount of recharge. All the tests were performed in air, and those cell packs cycled at 273 and 323/313 K (0° and 50°/40° C) were in temperature-controlled chambers. The cell packs at 298 K (25° C) were in an air-conditioned room. The ambient temperature quoted is believed to be accurate to within 2 K (2 C°).

Those cells that passed the acceptance tests were arranged in 5- and 10-cell groups. Each group had its own solid-state current-controlling unit to control the charge rate both in the constant-current mode and in the constant-voltage mode after the preset voltage limit had been reached. These two charging modes were achieved by regulating the current supplied with a 28-V dc generator common to all units. Relay switching systems changed the loads in the units to affect discharges. Auxiliary equipment scanned every cell on test once every 2 min. When any cell voltage rose above 1.7 V or fell below 0.5 V, the equipment sounded an alarm and disconnected that cell from the charge/discharge control circuits. If more than half the cells in a group failed, the entire group was said to have failed.

Disconnected cells were subjected to a failure analysis procedure performed at QEL. The manufacturers had the option of participating if they wished. This arrangement had the advantage that a common failure analysis procedure was applied to each cell. Consequently, greater uniformity was obtained in evaluation and interpretation. The failure analyses were successful in indicating to several manufacturers where improvements could be made in cell design and materials.

Data for the cells on test were obtained and recorded on punched paper tape approximately every 32 cycles for the 1.5-hr cycle, every 16 cycles for the 3-hr cycle, and every 8 cycles for the 24-hr cycle. The parameters measured were group current, voltage, and temperature and individual cell voltages. The maximum number of cell groups that could be measured simultaneously was 18. A computer converted the data to obtain amperes, volts, and degrees Celsius. This information was stored on punched cards for evaluation. About

Table 1—*Combinations of parameters and ambient temperatures used in QEL tests.*

Ambient Temperature (K)	Depth of Discharge (%)	Amount of Recharge (%)	Charge Voltage Limit per Cell (V)
273 (0° C)	15, 25	115	1.55
298 (25° C)	25	125	1.49
323/313 (50°/40° C)	15, 25	160/140	1.41/1.45

every 88 cycles, a capacity check was made on each cell, but these data were not integrated with the above measurements.

This NASA program gave more tangible results than the previous program because of better organization of the tests and subsequent analyses and because of more efficient data collection. Subsequent analysis of these data, which will be discussed later, has yielded much additional useful information and has led to techniques of predicting cell failures during a test. The disadvantages of the program include the fact that it is costly, and the results may already be outdated when they become available. However, as noted previously, these disadvantages are characteristic of many operational life tests. The capacity check about every 88 cycles was found to condition the cell and thus to lead to an extended cycle life. No controls were run to determine the effects of the capacity checks. However, it was noticed that after such a check, the cycle behavior took considerable time to return to that observed prior to the test. (Further details may be found in Reference 15.)

The original tests at QEL have been extended to include a wider range of cells of more recent manufacture. These include silver-cadmium cells, silver-zinc cells, and cells with different types of charge control devices. Thus, the program is producing information on recently available cells even though the test procedures have been changed very little from those described. To accommodate the different electrical characteristics of these newer cells and to cover a wide range of anticipated environmental conditions, the temperature range has been extended to 253 K (−20° C), the depth of discharge range has been extended from 10 to 75 percent in some cases, and an 8-hr cycle period has been introduced (1-hr discharge, 7-hr charge) with a recording frequency of 12 cycles (Reference 16). At the present time, operational tests are still being performed, and the results are being published annually. (See the bibliography.)

Wright-Patterson Air Force Base

The Wright-Patterson Air Force Base battery evaluation program is currently being operated by the Columbus Laboratories of Battelle Memorial Institute at the Aero-Propulsion Laboratories, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(615)-3701. The object of this program is to investigate the performance characteristics and establish the optimum operational parameters for spacecraft batteries operating for 3 to 5 years in simulated polar and synchronous orbits.

Because the emphasis in this program is placed on obtaining operational parameters under simulated orbit conditions, care was taken in devising the acceptance and cell-matching tests to use procedures common to those practiced by manufacturers in qualifying their batteries for actual missions. The actual operational cycling tests were also designed to match expected orbital mission requirements.

A detailed description of the test procedures and the test equipment is given in References 17 and 18. A brief description of this work is given below.

Preliminary acceptance and cell-matching tests were used to condition the nominal 20-A-hr, sealed nickel-cadmium cells. This was done to verify the performance data given by the manufacturers and to obtain the information necessary to match the cells closely for the simulated-orbit tests. Matching was based upon measured capacity and end-of-charge voltage after the cells had been checked for physical and electrical defects.

A total of 25 cells from each of four manufacturers was tested in the above manner in order that four groups of 10 cells could be placed on the life test proper; each group of 10 cells was selected from one 25-cell group. Two of the four groups were tested under a simulated polar orbit regime of 5.31 hr, whereas the other two groups were tested under a simulated synchronous orbit regime of 24 hr. These two regimes are shown in Figures 1 and 2. Both sets of groups were mounted on a heat-sink platform and cycled in an environmental chamber held constant at 298 K (25° C). Some of the cells placed on test had pressure transducers affixed; others had dummy tubes of equal volume.

Thus far, two important differences between this test procedure and those described earlier are apparent. First, the cells were matched as far as possible for electrical performance to minimize the effects that varying operational
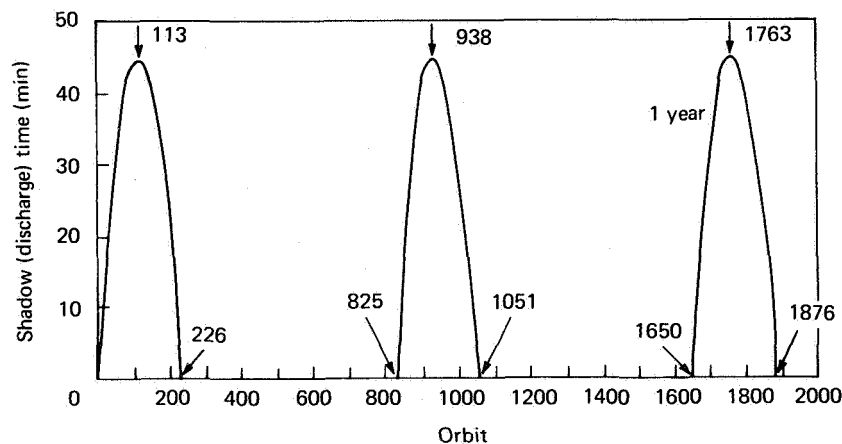
Figure 1—Simulated 9260-km (5000-n. mi.) circular polar orbit. Each 10-cell group evaluated under the polar orbit conditions was alternately charged and discharged for 225 cycles, with the discharge time ranging from zero for the first cycle to a maximum of 45 min on the 113th cycle and back to zero on the 225th cycle in such a manner that the discharge time, as a function of cycle number, approximated a sinusoidal function. The total time per cycle was a constant value of 5.31 hr. The remaining time per cycle not accounted for was used for charging. At the completion of 225 cycles, the cells were subjected to continuous charging for 599 cycles (3180.7 hr). After the completion of 599 cycles, the 225-cycle discharge routine was repeated.
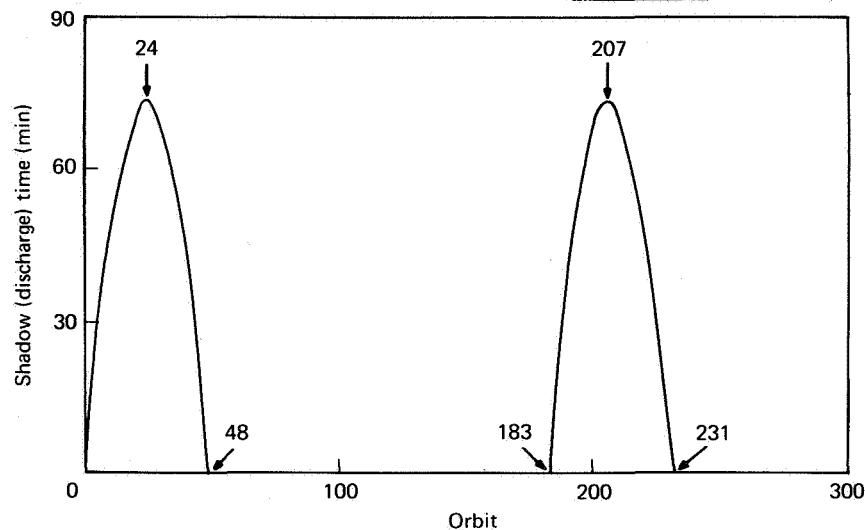
Figure 2—Simulated synchronous equatorial orbit. Each 10-cell group evaluated under the equatorial orbit conditions was cycled in the following manner. Each cycle was 24 hr in length, and the cells were alternately charged and discharged for a total of 48 cycles. The discharge period ranged from zero on the first cycle to a maximum of 74 min on the 24th cycle and returned to zero on the 48th cycle in such a manner that the discharge time, as a function of cycle number, approximated a sinusoidal function. Upon completion of these 48 cycles, the cell group was subjected to a continuous charge for 135 cycles, after which the 48-cycle discharge routine was repeated.

characteristics might have on cell life. Second, a fixed charge/discharge cycle regime was not used. Instead, the time duration of the charge and discharge periods varied according to the load cycle of the associated simulated orbit. Moreover, the depth of discharge was controlled to a maximum preset limit of 80 percent.

All charges and discharges were made with constant current. A two-step charge was used, with the switch from a high-rate to a low-rate charge occurring when the group voltage reached 14.5 V (about 1.45 V per cell). There were preset voltage limits outside which a cell was classed as "failed." An automatic warning device indicated when a cell exceeded tolerances and removed it from the circuit. The operator then had a choice of placing the cell back into the circuit or removing it and performing a failure analysis.

Data were recorded every 2 min during the discharge portion and during the first part of the charge portions of selected cycles in the eclipse portion of the test regimes. The cycles were selected to give the maximum amount of useful information with a minimum amount of punched tape from the data console. The data include individual cell voltages, temperatures, and pressures (where applicable); group currents and voltages; and heat-sink base plate temperatures. Thus, this test was primarily oriented to give data for individual cells while

monitoring only group properties. Data on punched tapes were transferred to magnetic tape to be used with a computer program designed to print desired information in tabular form.

To date, after more than a year of continuous testing, only one cell has failed. Consequently, specially designed failure analysis procedures have not yet been validated in this program. Although the orbital tests were not designed to be accelerated tests, it may be possible in terms of an accelerated test to analyze the comprehensive data once the appropriate stresses and strains are identified.

Union Carbide Laboratories

The battery evaluations of Union Carbide Laboratories, Parma, Ohio, are basically in-house research carried out for the evaluation and analysis of the manufacturer's own products (Reference 19). The cycling facilities consist of equipment capable of programmed charges and discharges of up to 5 A for 12-cycle regimes with a maximum of 16 cells in each regime.

Union Carbide Laboratories uses a computer to control cycling tests and for data collection and analysis. The computer is used to select the charge and discharge times; also, it can select any one of four preadjusted charge or discharge voltages. The computer scans the measurement points every 36 s. A reading is recorded if the difference between the present reading and the last reading is greater than a variable threshold; each time a reading is taken, this variable threshold is determined by taking the difference between the last recorded reading and the present reading and dividing this difference by the number of measurement points that can still be recorded out of the original limit of 10 (Reference 19). The idea is to record only those data points that convey the most information. For example, in the measuring of a discharge curve, the greatest changes in voltage per unit time base occur at the beginning and at the end of the discharge. The computer recognizes this and gives a high density of recording points in these areas. On the other hand, during that part of the discharge when the voltage changes very little (the plateau), the computer records a minimum number of data points. At the end of any charge/discharge cycle, there is an option to store the information on magnetic tape or to erase the memory.

The cycling facility can be programmed to measure for each cell on each cycle the ampere-hour capacity, watt-hour capacity, ampere-hour efficiency, and various other parameters in addition to the charge and discharge voltages. There is also provision to measure cell temperature and pressure, although this has not yet been implemented. Most tests currently being performed are cycle tests at room temperature, although environmental testing may be performed if desired.

This example of an operational life test is the most sophisticated of those considered, at least as far as instrumentation application and utilization is concerned. However, because of the 5-A limit, there is a limit to the number
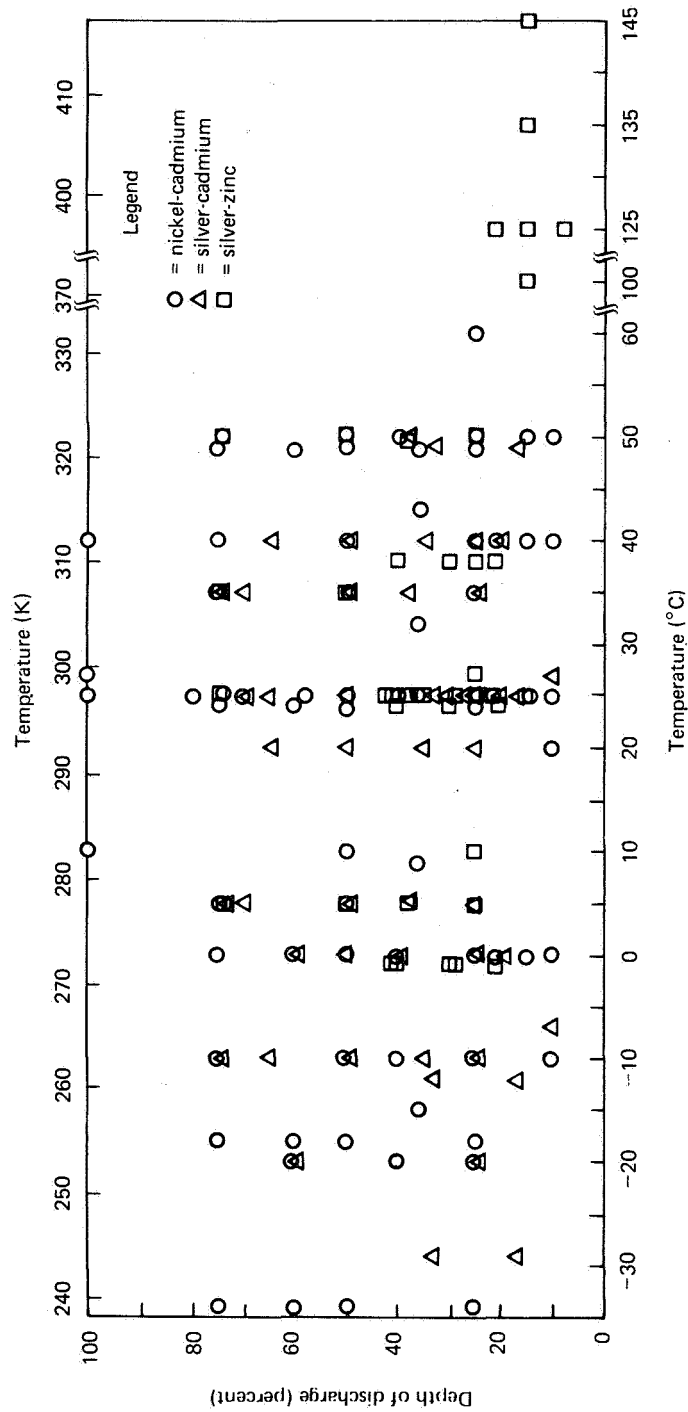
Figure 3—Various combinations of temperature and depth of discharge used in the life testing of spacecraft cells.

and type of cells that can be tested and to the rates at which the cells may be cycled.

No accelerated tests were originally planned for the facility. However, as will be discussed later, the rate of change of certain parameters (such as voltage) is being used to predict cell life. A graphic record of the changes of the parameters of interest may be obtained; thus, if different stress levels are introduced into the cycling regime, observation of the rate of change of the parameters could form the basis of an accelerated test.

Experimental Conditions Used in Operational Life Testing

Previous paragraphs have described examples of different types of operational life tests and their implementation. In Appendix A, some of the other experimental conditions used in testing spacecraft cells are tabulated according to the three cell types: nickel-cadmium, silver-cadmium, and silver-zinc. The information has been condensed to give the testing facility contract number, orbit or cycle type, temperature, and depth of discharge. Thus, the appendix suggests the experimental conditions that have been used.

Although limited, the appendix encompasses a broad range of the available literature published over the past 7 or 8 years.

Figure 3 shows a plot of the various combinations of temperature and depth of discharge for the references used in.the appendix. In most instances, the reference associated with a specified point in the plot can be easily identified by referring to the appropriate table for nickel-cadmium, silver-cadmium, or silver-zinc cells.

FAILURE ANALYSIS PROCEDURES

In the operational life tests described, analyses of the failed cells are important for identifying the failure determinants, which are defined below. Such studies could lead to improvements in cell design and manufacture and, subsequently, result in prolonged life.

Simple failure analysis procedures were used in the Inland Testing Laboratories program; more sophisticated procedures, with a high degree of standardization, were used in certain QEL programs (References 20 and 21) and in other programs (Reference 22). More recently, special procedures for the failure analysis of silver-zinc and nickel-cadmium spacecraft batteries have been devised by Battelle's Columbus Laboratories (References 18 and 23). The procedures consist of three parts, patterned after medical examinations and autopsies. First, there are instructions to record the previous history and physical condition of the cell. These include visual observations; determination of weight, presence of cracks, and electrolyte leakage; and internal short tests. Second, there are instructions to determine the electrical characteristics of the cells. These instructions, for example, call for performance tests and capacity

determinations. Third, there are instructions for cell disassembly and examination to determine the condition of the electrodes, separators, and other internal cell components.

The failure mode is known from the failure history of the cell; therefore, the purpose of the failure analysis procedure is to identify the failure determinant. However, the failure analysis procedure is not designed to identify failure mechanisms, although the identity of some of these mechanisms may be inferred from the observations and measurements made.

Several terms used in the above paragraphs have been given precise definitions (Reference 18). These definitions were found necessary because of the vague and ambiguous manner in which these terms are used in the literature. These proposed definitions are listed below because they are believed sufficient to include meanings given to terms such as failure causes, characteristics, modes, mechanisms, analyses, reasons, antecedents, factors, fashions, way, symptoms, and similar phrases. (See Appendix B for a more complete glossary of terms.)

Failure: The failure of a secondary cell is its inability to deliver on discharge, or to accept on charge, a preselected quantity of electrical energy under a specified set of environmental conditions. Thus, if the user decides that the electrical parameters are outside of desired limits, the cell is said to have failed.

Failure mode: The failure mode is a particular manifestation of failure, such as a voltage lower than desired on discharge. A failure mode has dimensions of the parameter that went out of tolerance (e.g., voltage, current, and time).

Failure determinant: The primary cause of the failure mode is defined as the failure determinant. Thus, the failure determinant is an immediate cause for voltage, current, or time going out of tolerance. For example, a failure mode of low discharge capacity (current and time out of tolerance) may be the result of a loss of active material, the failure determinant. The word "determinant" is chosen because of its preferred dictionary meaning: "A cause that fixes the nature of what results as an outcome."

Failure mechanism: A failure mechanism is the fundamental physical or chemical process that contributes to producing the failure determinant. A knowledge of failure mechanisms is desirable for understanding cell failures, but knowledge of failure mechanisms is not necessarily essential in a failure analysis procedure, which is usually concerned with failure determinants.

Failure analysis procedure: A failure analysis procedure comprises a collection of physical, visual, electrical, and chemical tests arranged in such a manner as to lead to an explanation of the determinants of a failure mode.

In summary, these definitions form a hierarchy in which the failure mechanisms give rise to failure determinants that lead to failure modes and thus describe failure. The definitions describe a direct cause and effect relationship between each level in the hierarchy. This hierarchy should be taken as a structural description of possible failures, with the different levels in the structure used to interpret failure according to the level of sophistication desired.

In the QEL reports, a description of the failure analysis procedures applied to failed cells is given. Waite and Epstein (Reference 24), in reducing the operational life data for empirical analysis, included a list of the failure characteristics. This list of 21 characteristics for nickel-cadmium cells is given in Table 2. It should be noticed that the list contains both failure modes and failure determinants and is thus an example of the ambiguity in reporting that has occurred with failure analysis. Items (A) and (B), for example, are failure modes, but most of the other characteristics are difficult to relate directly to electrical parameters and thus do not fit into the hierarchy of causes and effects.

Under Contract AF 33(615)-3701, Battelle's Columbus Laboratories reviewed much of the literature on failure analysis tests (Reference 18) and, using the background information given above, came to the following conclusions. Among nickel-cadmium batteries, or cells tested beyond 4000 charge/discharge cycles, most failures resulted from mismatched voltages, memory effects, or internal shorts. Practically all failed cells showed evidence of high internal pressure, such as bursting, loss of electrolyte through leaks, and bulged cases. Many of the cells that failed because of memory effects could be restored to operational use by deep cycling, such as during the determination of the capacity of the cell or during a check for internal shorts.

Table 2—*Summary of the failure characteristics for nickel-cadmium cells observed in the QEL test program.*

Designation	Failure Characteristic
(A)	Low voltage on charge
(B)	Low voltage on discharge
(C)	Defective separator (deteriorated, dissolved, burned, pinpoint penetration, shorted)
(D)	Plate material shorted through separator
(E)	Separator impregnated with negative plate material
(F)	Migration of positive or negative plate material
(G)	Extraneous material between plates
(H)	Deposit on positive or negative terminals
(I)	Blistering on positive plates
(J)	Plate stuck to case
(K)	Excess scoring of case
(L)	High pressure, bulge, convex sides
(M)	Concave sides, shorts due to internal shift
(N)	Broken seals (ceramic or glass)
(O)	Ceramic short
(P)	Electrolyte leak, weight loss, dry separator, cell shorted by electrolyte
(Q)	Defective tabs (burned, broken, welds weak)
(R)	Third electrode shorted to plate
(S)	Burst cell
(T)	Short circuit, open circuit
(U)	High voltage on charge

Table 3—*Summary of an analysis of reported battery failures.*

Type of Battery	Failure Mode[a]			Failure Determinant	Possible Failure Mechanism
	Charge	Charge/Discharge	Discharge		
Nickel-cadmium	$+V$		$-V$	Memory	Temporary passivation
		$+V/I$		High impedance	Material migration, electrolyte loss
		$-V/I$		Shorts	Separator deterioration, inferior quality control
	$+V, +I$			Leaks, bursting	Overcharging
		$-It$	$-V, -t$	Loss of active material	Permanent passivation
		$-I, \pm t, -V$		Defective structure, impurities	Side reactions, inferior quality control
Silver-zinc		$-IVt$		Loss of active material	Migration, passivation
		$-V/I$		Shorts	Dendrite formation, separator deterioration
	$+V$		$-V, -t$	Leaks, bursting	Overcharging
	$-I$		$-V, -t$	Defective structure, impurities	Side reactions, inferior quality control

[a]Failure mode indicates undesired value of current I, time t, or voltage V. Plus sign (+) indicates excessive magnitude; minus sign (−) indicates deficient magnitude.

In life tests for silver-zinc cells, excessive pressure and bursting were also evident in reported failures, but the most common failure determinants were internal shorts and loss of negative electrode capacity.

A summary of published failure modes (Reference 18) is given in Table 3, which provides a more definitive set of failure determinants, thus reducing the chance of ambiguous interpretation. The newer terminology is suggested as an improvement over the listing and terminology used in Table 2. In Table 3, six of the more important failure determinants are listed, in contrast to the 21 failure characteristics listed in Table 2.

Because of the differing electrical and physical characteristics of the various types of electrochemical energy conversion devices, it would be unwieldy to devise one failure analysis procedure applicable to all types. Different procedures for different cell types are, therefore, desirable. Standardization of each procedure will, then, be advantageous in that results from different manufacturers will be comparable.

OTHER TESTING METHODS

Testing methods applicable to spacecraft battery evaluation also include the so-called acceptance tests and screening tests. Before starting any operational or accelerated life test, it is customary to perform certain tests to insure that the batteries are of high initial quality and possess desirable characteristics. It is these tests that are usually referred to as acceptance tests and screening tests; this relationship is graphically shown in Figure 4.

Because these tests are usually tailored to each individual application and to each individual cell, general descriptions of the tests are not easily given. Therefore, only the distinction between the tests and the general nature of these tests will be described. For details of individual test procedures that have been used, the reader is directed to the extensive collection of titles in the bibliography.

Acceptance tests are usually performed to insure that the cells satisfy the manufacturer's specifications. Acceptance tests often involve physical examinations, which may include taking X-ray photographs and checking the dimensions of the cell. The tests may also involve the disassembly of sample cells to check on the quality of the manufacturing process.

Screening tests are often intermediate between acceptance tests and operational or accelerated life tests. For example, an accelerated life test may require that all cells be matched as closely as possible before the test is run. This not only entails the performance of acceptance tests on the type of cell selected but also involves procedures such as cell conditioning and controlled charge/discharge cycling to allow the electrical characteristics of the cells to be matched as closely as possible. Through use of this screening test, atypical cells can be screened out, thus eliminating their adverse effects on subsequent tests. In essence, all operational life tests are reliability tests for the chosen set of conditions because both kinds of tests determine the life of the cells.

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         ┌──────────────┐    ┌──────────────┐
         │  Acceptance  │    │   Screening  │
         │    tests     │    │    tests     │
         └──────────────┘    └──────────────┘
                │              │         │
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                │  ┌──────────────┐    ┌──────────────┐
                │  │Nondestructive│    │  Destructive │
                │  │    tests     │    │    tests     │
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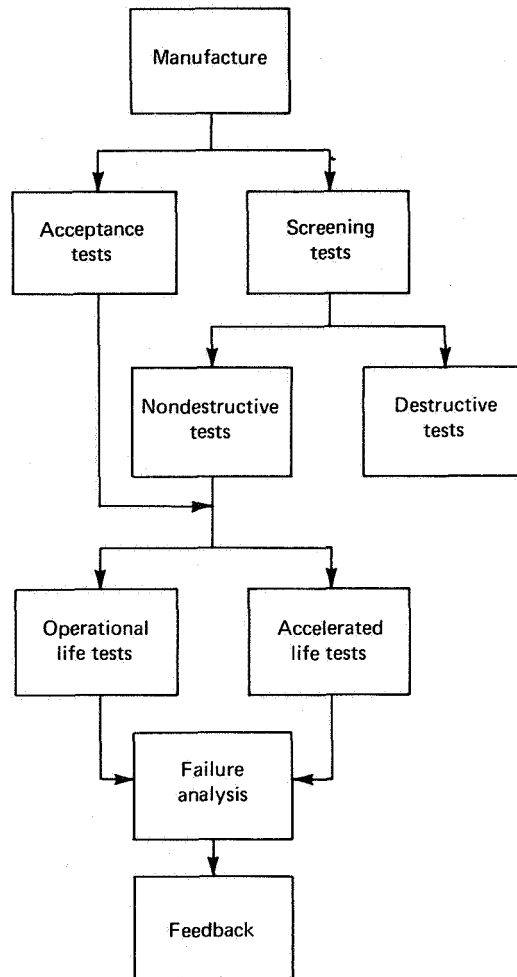
Figure 4—Various forms of spacecraft battery testing related to accelerated life tests and failure analysis procedures.

Various other tests have been devised for more specific purposes and are described in the literature. Some of these, such as the "upside-down" test and "tests to failure," are briefly described below to further indicate the scope of the methods used in battery testing.

The upside-down cycle test for nickel-cadmium cells, described by Sherfey (Reference 25), is an operational life test based upon a 65/35-min charge/ discharge cycle. The characteristic that distinguishes it from operational life tests is a "bleed" cycle every fifth cycle. In this bleed cycle, a low-value resistor is connected across each cell for the next complete cycle so that the cell is almost completely discharged. The main advantage of this technique would

seem to be that cell memory effects are avoided by the reconditioning that occurs. Data indicate a longer cycle life, although no controls were run to justify this conclusion.

The upside-down cycle tests were performed at 283, 298, and 313 K (10°, 25°, and 40° C); progressively shorter cycle lives were obtained at each higher temperature. If the failure mechanisms remain the same with change in temperature, the basis for a valid accelerated test may exist. However, because the upside-down cycle procedure conditions the cell, a similar set of experiments without the bleed cycle would yield a reduced cycle life and would constitute an accelerated test, provided the failure mechanisms are the same.

Step-stress tests to failure have been recommended in the past by the U.S. Army (Reference 26); the advantage of the step-stress test-to-failure concept, as compared with operational life tests, is that a high reliability can be established with reasonable confidence on the basis of a small number of samples. A step-stress test to failure involves submitting a test specimen to a programmed, incrementally increased stress until failure occurs. A lower limit of stress below which the probability of failure is sufficiently small can be selected by using appropriate means and standard deviations of the data generated by such tests. These tests, as described for thermal batteries by Langlie (Reference 26), are thus a form of reliability test; however, because of the time compression obtained through using increasingly severe levels of stress, an accelerated life-test framework may also exist.

The disadvantage of the step-stress method (or the corresponding continuously increasing stress method) is that often there is little proof that the failure mechanisms at operational levels are the same as those at higher stress levels. The validity of the threshold value of the chosen stress level is, then, open to question.

Factorial designs and fractional factorial designs have been introduced into the testing of electrochemical energy conversion devices (References 2 and 27) for use in evaluating improvements in design, construction, and materials and in the testing of solar cells for space application. When a large number of independent variables is involved, fractional factorial designs may be used to determine the minimum number of tests required to obtain useful data. For example, in the preliminary screening of various sealed silver-zinc cell components (Reference 2), only 200 cells were required to evaluate approximately 25 different separator systems, plus several levels of concentration of four negative-electrode binders, three surfactants, and three voltage additives. In addition, experiments with these cells also allowed the evaluation of the zinc-to-silver ratio, zinc-to-zinc-oxide ratio, positive-electrode density, and electrolyte concentration and quantity. The time and cost saved in these screening experiments can be readily appreciated.

The drawback with fractional factorial designs is that little information is obtained on some of the interaction effects on cell life. Fractional factorial experimental designs may achieve a reduction in the number of cells required

for testing; however, the price for this reduction is an increased risk of failure in obtaining information on important interactions. Further discussion of the advantages and disadvantages is given in Reference 28.

Various other tests, some designed to measure specific characteristics, have been applied to spacecraft cells. For example, double-layer capacities (Reference 29) and internal impedances or resistances (Reference 18) have been measured in situ in efforts to characterize electrodes and cells. Changes in pressure and surface area have been measured and used in conjunction with evolved-gas analysis (Reference 29) to help describe operating characteristics. Empirical tests, such as application of an ac pulse to an operating cell to screen bad cells, have also been used.

For several reasons, pulse techniques (or other methods for measuring fast transients), such as those described above, appear to be advantageous for an accelerated test procedure. First, because of the short duration of the pulse and its possible intermittent application, the volume of data required for analysis would be relatively small. Second, the time response to the transients might provide some convenient measure of the rate of degradation of quality. A large or small hysteresis occurring in response to a pulsed stress and found to be closely related to the rate of degradation of quality would appear to be a useful criterion in an accelerated test. Third, a short accelerated test might be obtained at a low average stress level through the application of pulsed stresses of relatively more severe nature and analysis of the resulting transients. However, the problem of determining whether the failure mechanism is unchanged remains.

3 EMPIRICAL APPROACH

Some of the differences between empirical, statistical, and physical approaches to the analysis of accelerated test data have been discussed. In the empirical approach, the data may be regarded as containing unknown relationships embedded in noise; analysis of the data consists of a search for structure. Moreover, the search is made with minimal assumptions regarding the kinds of structure that may be present. Through application of a wide variety of code-cracking techniques, the data are processed in a way that will reveal interesting structure. The exact sequence of analysis is not predetermined; instead, the kind of analysis made at each stage depends on what kind of structure has been extracted prior to that stage. Because smoothing may suppress interesting structure, the empirical analyst tends to smooth as little as possible. After interesting structures are identified in the data, statistical methods are applied to assess the persistency of the structure in the noise background. Persistent structures are then recommended to the statistician or physicist for further study.

Because most data-processing methods involve a considerable amount of smoothing, few techniques are available for empirical analysis. The methods of nonparametric statistics and certain classification techniques, such as AID, offer some acceptable methods.

The exact sequence for using empirical methods need not be specified in advance. In general, whenever an interesting aspect of the data has been exposed, the empirical analyst attempts to exploit this aspect further by whatever methods seem appropriate. This means that the resulting analysis is sequential and dependent upon the data. Rarely would the same sequence of methods be applied to different sets of data.

The empirical analyst searches for relations by purely numerical methods. Typically, these methods involve processing the data through a blend of procedures based on a variety of classifications, histograms, marginal distributions, rank correlations, and combinatorial structures. The associations need not be explained; they are simply exhibited. The explanations of the detected associations are left to the physical chemist.

Because the smoothing, or averaging, of data causes a loss of information, the empirical analyst usually begins by processing the data in its raw form. For this reason, he generally detects errors, inconsistencies, and suspicious "outliers."

After removing identified discrepancies, he is able to search for more subtle features of the data. Only when these features persist with operating time is the analyst ready to average the data and claim that some structure has been detected.

One of the important functions of empirical analysis arises in the monitoring of data as they are generated. Again, those methods that are suitable for detecting errors and outliers serve as good tools for maintaining a high level of data quality. By online monitoring of the data, suspicious behavior in the measured values may be identified quickly and corrective measures may be taken if appropriate. Such monitoring usually does not require a knowledge of the physics of the cell or even of statistical quality control. Monitoring merely requires a well-planned supervision of the generated numbers. The characterizations of typical data behavior can be established by empirical methods during early portions of the experiments. These characterizations may serve as quality-control criteria to be used as monitoring procedures during the remainder of the experiment. As discussed later, early changes in data so generated are to be used empirically for the prediction of failures.

EMPIRICAL PHILOSOPHY FOR ACCELERATED LIFE TESTS

The preceding considerations may be combined to form a general empirical philosophy for the conduct of accelerated life tests. The following discussion is aimed at exhibiting the important features of this point of view.

As noted earlier, the empirical analyst prefers some online monitoring of the data quality. In this way, concern with spurious results is alleviated. Secondly, the online monitoring can be computer based so that concurrent numerical analysis is possible. This means that distributions, histograms, and associations can be generated in a sequential way and used both to monitor the quality of the data and to study possibly persistent structures found to occur in the data. Gradual changes in the persistent structures may permit the prediction of behavior. In accelerated test applications, the aim is to predict the failure of a cell before the failure has actually occurred. This is the most convincing kind of prediction because it is not subject to the hindsight criticism that may be associated with postexperimental analysis of the data.

An additional assumption may be made that makes the empirical approach still more specific. The measured values of variables associated with a group of nominally identical cells operated at the same stress level are expected to show some typical behavior. Cells having measured values of particular variables or combinations of variables that deviate from the typical behavior may be said to occupy a "tail" of the distribution of behavior. One of the objectives of the online empirical approach is to identify typical behavior and tails. Those cells associated with a tail are put under suspicion; such cells are expected either to be poor cells and fail early or to be exceptionally good cells and fail late. In either case, these cells warrant more detailed surveillance. If possible, the rate

of data taking should be increased for cells in the tails, perhaps at the expense of taking fewer measurements on the cells associated with typical behavior. The increased monitoring rate may provide for the early establishment of trends; this, in turn, would be expected to permit predictions of behavior to be made more quickly.

Suppose the tails have been identified and are closely monitored over time but no failures occur and no failures have been predicted. If a failure of a cell occurs under these conditions, it is clear that all of the cells in that same tail should be predicted to be early failures. This can be done even if sufficient data have not been obtained to predict the times to failure. Moreover, if a cell associated with typical behavior fails, a reassessment of the conditions defining the tails may be appropriate. In summary, an empirical online monitoring of accelerated life tests may be structured to achieve the following:

(1) Establish and maintain a high level of quality for the data
(2) Identify persistent typical behavior and persistent tail behavior
(3) Increase the monitoring rate for cells showing persistent tail behavior
(4) Establish trends associated with gradual changes over time, with special emphasis on the tail cells
(5) Predict cell failures in persistent tails, based either on extrapolated trends for the tail or on the actual occurrence of a cell failure in the tail

In the context of an ideal accelerated test, a minimum of at least five stress levels should be used, for reasons explained in Section 4. The empirical monitoring of the generated data would be carried out at each level of stress. This procedure would permit early study of possible relationships of tails within stress levels and between stress levels. As a result, early predictions may be provided for the behavior at a lower stress level from the observed behavior at a higher stress level. One method for accomplishing early predictions involves "parametric" failures. This approach is described in Section 9.

APPLICATION OF THE AID PROGRAM TO QEL DATA

As an example of an empirical analysis, the AID computer program is applied to failure data obtained at QEL. The data are documented in a report by Waite and Epstein (Reference 24).

Table 2 shows a QEL listing of the 21 failure characteristics generated by Waite and Epstein for the QEL data. The characteristics were not chosen for the purposes of making an AID analysis. In fact, as discussed in Section 2, the Waite-Epstein classification contains both failure modes and failure determinants; consequently, the list is not well suited to either empirical or theoretical analysis. Nevertheless, an empirical study can be made to determine whether any of these failure characteristics are closely associated. The data serve primarily as a basis for illustrating the empirical approach.

Description of the AID Program

The AID program is a computer program for identifying which independent variables are the best predictors of a given dependent variable. In an accelerated test application, recommended variables would be voltage quality, temperature quality, or pressure quality (Reference 1), as described in Section 5. The independent variables consist of any measured values that are possible predictors of quality.

The AID program begins by determining how well each independent variable can predict high or low values of the dependent variable. If one of the independent variables is found to be perfectly associated with the dependent variable, the data set is "split" using this independent variable. In the simplest case, suppose that the dependent variable y can take only the values of 0 and 1. Further, suppose that there is an independent variable x_1 that also takes on values of 0 and 1, and suppose that $y = 1$ whenever $x_1 = 0$ and $y = 0$ whenever $x_1 = 1$. In this case, x_1 is a perfect predictor of y. That is, given that $x_1 = 0$, y is always found to be 1; and given that $x_1 = 1$, y is always found to be 0. The AID program would identify x_1 as a good predictor of y and would split the entire set of data into two groups. In the first group, all the data for which $x_1 = 0$ would be included; in the second group, all the data for which $x_1 = 1$ would be included. Thus, the initial data (in one group) are split into two groups. It is convenient to represent such a split by a "tree," as shown in Figure 5.

If perfect predictors cannot be found, the AID program simply identifies whatever predictor is best and splits the data using the best predictor. In quantitative terms, the best predictor is that independent variable which maximizes an F-ratio. In intuitive terms, the F-ratio is the ratio of the statistical variability of y that is accounted for by the variability of x_1 to the variability of y that is not accounted for by the variability of x_1. If all the variability is accounted for, the F-ratio is infinite; if none is accounted for, the F-ratio is zero. Thus, the AID program simply computes the F-ratios associated with each independent variable and splits the data using the variable that yields the maximum F-ratio.
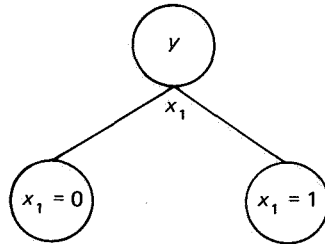

Figure 5—Simple example of an AID tree.

Many other features associated with the AID program are given in Reference 30. The description given here is generally all that is needed to explain the following illustrative examples.

Examples of AID Applications to QEL Data

Figure 6 shows a portion of one of the trees that results when the AID program is applied to the QEL data. This particular tree is obtained when failure characteristic (B), low voltage on discharge (from Table 2), is used as a dependent variable and the other variables in Table 2 are used as predictors. In the node at the top of the figure, the ratio 280/377 appears; this ratio shows that failure characteristic (B) occurs 280 times in a total of 377 cases of cell failure.

It is seen in Figure 6 that the variable most strongly associated with (B) is (T); the F-ratio associated with this split is 52.96 and is shown beneath the symbol (T). The split shows that the initial 377 cases are divided into 275 cases and 102 cases, corresponding to the denominators of the fractions shown in the left and right nodes, respectively. For convenience, the absence of a failure
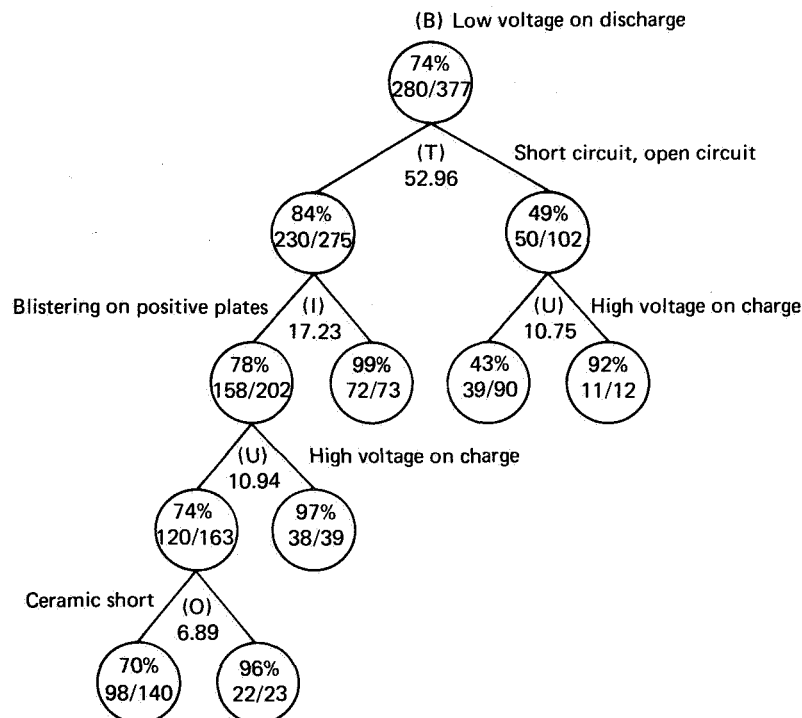

Figure 6—AID tree, with F-ratio, for predicting low voltage on discharge.

characteristic is associated with the left branch of the split, and the presence of a failure characteristic is associated with the right branch. Thus, the two nodes obtained with the first split give the following information:

(1) Out of 275 cases in which (T) was absent (no short or open circuits), 230 of these had low voltage on discharge.

(2) Out of 102 cases in which (T) was present (a short or open circuit), a total of 50 showed low voltage on discharge.

The AID program examines these two groups and determines which variables are the best predictors for these groups. For example, the right node, formed by the split on (T), was split further on the basis of variable (U), high voltage on charge. The split on (U) gives the following information:

(1) There were 90 cells in which (T) was present and (U) was absent (that is, a short or open circuit was present, and a high voltage on charge was absent). Of these 90 cells, 39 showed low voltage on discharge.

(2) There were 12 cells in which (T) and (U) were both present (that is, either a short or open circuit was present, and a high voltage on charge was present). Of these 12 cells, 11 showed low voltage on discharge.

Figure 6 also shows additional branches of the tree that were obtained when splits were made using (I), blistering on positive plates, and (O), ceramic short. In summary, this tree shows that the failure characteristics that serve as the best predictors of (B) are the variables (T), (I), (U), and (O). None of the other variables from Table 2 appear in Figure 6 because their F-ratios were lower.

As this example shows, the AID tree yields a set of conditional predictors. The conditions are associated with the nodes traversed by a path from the top of the tree to a terminal group. Although the tree generated in this example shows that (T) is the best predictor of (B), it does not follow that (B) is the best predictor for (T). That is, a predictive relation may not be symmetric; it will be shown how the AID program can be used to detect symmetric associations among variables.

An Empirical Search for Association

The AID program may be used to make an empirical search for association among variables. To exemplify one approach, the following steps were carried out:

(1) The AID program was run to predict the presence of (A), low voltage on charge, and a large tree involving 125 groups was obtained. An examination of F-ratios showed that the following variables yielded statistically significant splits: (B), (E), (I), (L), (O), (T), (U), (C), (H), and (P).

(2) A modified version of the AID program was run to obtain the variables least important as predictors of the presence of (A). In this case, large

F-ratios were obtained at the end of the branches, and the following variables were found to yield significant splits: (B), (E), (I), (L), (O), (T), (U), (N), and (D).

(3) The seven common variables ((B), (E), (I), (L), (O), (T), and (U)) were then run, with each variable in this group serving, in turn, as the dependent variable and the remaining variables serving as the independent variable.

(4) The following matrix was obtained by identifying the best predictor for each variable:

Variable	Predictor						
	(B)	(E)	(I)	(L)	(O)	(T)	(U)
(B)						X	
(E)				X			
(I)					X		
(L)			X				
(O)						X	
(T)	X						
(U)	X						

The X in the top row of the matrix shows that the best predictor of (B) (row 1) is the variable (T) (column 6); this is indicated by (B) → (T), which is read, "(B) is predicted by (T)." From row 6, it is seen that the best predictor of (T) is (B), so that (T) → (B). Thus (B) and (T) are mutual predictors; this is indicated by (B) → (T) → (B). In a similar way, row 2 shows that (E) → (L); row 4 shows that (L) → (I). It is found that

$$(E) \rightarrow (L) \rightarrow (I) \rightarrow (O) \rightarrow [(T) \rightarrow (B) \rightarrow (T)].$$

The last three letters are enclosed by brackets to indicate that the predictors of (E) are now "trapped" to the letters (B) and (T). By continuing in this manner, the following summary is obtained for the variables associated with the seven rows:

(1) [(B) → (T) → (B)].

(2) (E) → (L) → (I) → (O) → [(T) → (B) → (T)].

(3) (I) → (O) → [(T) → (B) → (T)].

(4) (L) → (I) → (O) → [(T) → (B) → (T)].

(5) (O) → [(T) → (B) → (T)].

(6) [(T) → (B) → (T)].

(7) (U) → [(B) → (T) → (B)].

These results show that, no matter what variable is to be predicted, the resulting sequence of best-predictor variables always terminates with the associated variables (B) and (T). A similar analysis may be based on the second-best predictors, and the results show that the set (I), (E), and (O) are

associated variables. Together, these analyses suggest that low voltage on discharge (B) and short or open circuits (T) comprise the best set of associated predictors for the entire set of failure characteristics. After the effects of these variables are taken into account, the next best set of associated predictors consists of blistering on positive plates (I), separator impregnated with negative plate material (E), and ceramic shorts (O).

It should be reemphasized that these findings are given merely to exemplify one recent computer-based method of deducing empirical associations. Several other methods are available, including an extension of the trigram method (Reference 10). Having detected associations by any of these methods, it remains for the statistician to assess the statistical significance of the association, and it remains for the physical chemist to assess the physical meaning of these associations.

Summary of AID Trees

The seven AID trees used in the search for association are described in more detail in this section. Only the statistically significant portion of each tree is presented. A few observations then are made concerning some characteristics of each tree. In general, the terminal nodes are examined to determine which nodes are associated with high or low ratios.

Figure 6 shows the AID tree obtained for predicting the presence of failure characteristic (B), low voltage on discharge, for the QEL data on 377 failed cells. In each node, the upper number gives the percentage of the cells that show low voltage on discharge, and the lower numbers give the ratio of the number of cells that show low voltage on discharge to the total number of cells in the group. The top of the tree shows, for example, that (B) was present in approximately 74 percent of the 377 cells. The total number of cells having (B) present is shown by the numerator as 280. The best variable for predicting the presence or absence of (B) is seen to be (T), short or open circuit. Among the 275 cells for which (T) is absent, 230 of these, or 84 percent, have (B) present, as shown by the left node of the split on (T). The right node shows that when (T) is present, 49 percent of the cells have low voltage on discharge. The next split on failure characteristic (I), blistering on positive plates, shows that if (I) is present (right node) and (T) is absent, the observed frequency is 99 percent, and the cell will have low voltage on discharge. Similarly, the next split on failure characteristic (U), high voltage on charge, shows that if (U) is present, (I) absent, and (T) absent, 97 percent of the 39 cells in this classification have low voltage on discharge. Finally, the split on failure characteristic (O), ceramic short, shows that if (O) is present, (U) absent, (I) absent, and (T) absent, 96 percent of the 23 cells in this classification have low voltage on discharge.

It may be noted that the terminal nodes of the tree are composed of six groups having 98, 22, 38, 72, 39, and 11 cells with low voltage on discharge. The total of these numbers is 280, as shown in the initial node. Thus, the tree classifies the 280 cells having low discharge voltages into six groups of cells.

Three of these groups show high frequencies for the presence of (B) (96, 97, and 99 percent), and these three groups account for a total of $22 + 38 + 72 = 132$ cells out of the 280 cells in the initial group having (B) present. This indicates that low voltage on discharge can be correctly predicted with an observed frequency in excess of 95 percent for 47 percent of the cells having a low voltage on discharge.

Figure 7 shows the AID tree obtained for predicting the presence of failure characteristic (E), separator impregnated with negative plate material. This figure shows that 40 cells out of the total of 377 showed this characteristic. Further, if (L), high pressure, bulge, convex sides, is present, only 6 of 121 cells have the separator impregnated with negative plate material. In addition, if (O), ceramic short, is present, only 44 cells are involved, and only 2 of these have the separator impregnated with negative material. Thus, for this AID tree it is seen that if high pressure, bulge, or convex sides are present, it would be predicted that the cell would not have separators impregnated with negative plate material.

Figure 8 shows the AID tree for predicting the presence of failure characteristic (I), blistering on positive plates. Two nodes are of special interest in this tree. The first of these occurs at the bottom of the tree and corresponds to the left node of the split using (T), short or open circuit. This group of 35 cells may be characterized as follows:

(T) absent (no short or open circuit)

(B) absent (no low voltage on discharge)

(L) absent (no high pressure, bulge, or convex sides)

(O) absent (no ceramic shorts)

Among these 35 cells, none had blistering on the positive plates.
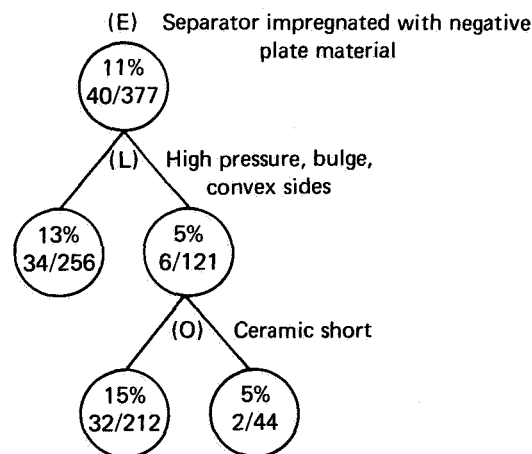
Figure 7—AID tree for predicting separator impregnated with negative plate material.

(I) Blistering on positive plates

24%
92/377

(O)   Ceramic short

21%
65/314

43%
27/63

High pressure, bulge,   (L)
convex sides

Separator impregnated
with negative plate
material

17%
35/212

29%
30/102

38%
22/58

100%
5/5

(B)   Low voltage on discharge

7%
4/59

20%
31/153

(T)   Short circuit, open circuit

0%
0/35

17%
4/24
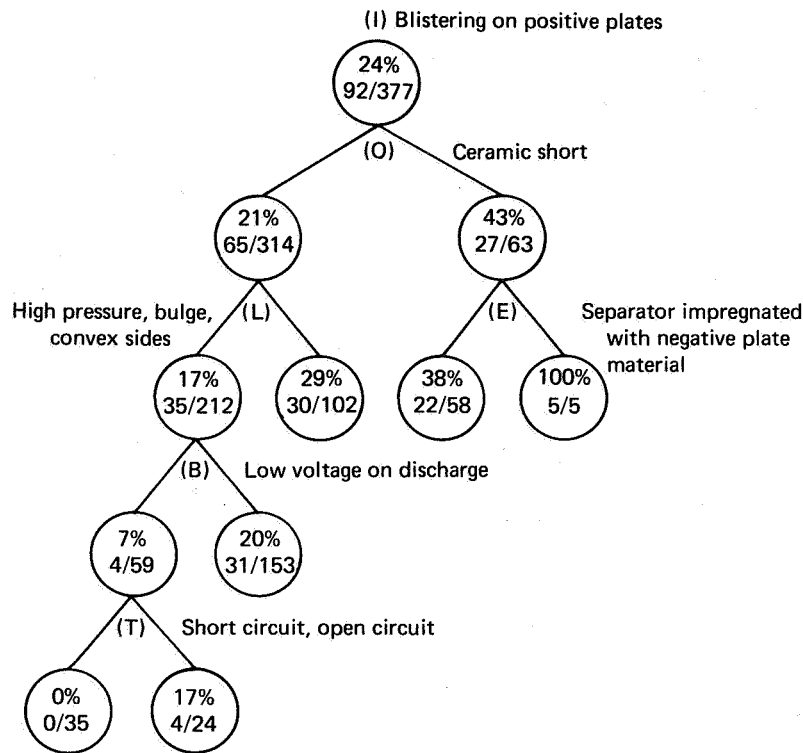
Figure 8—AID tree for predicting blistering on positive plates.

The split on (E), separator impregnated with negative plate material, shows that five cells had the following characteristics:

(E) present (separator impregnated with negative plate material)
(O) present (ceramic short)

Each of the five cells having (E) and (O) present showed blistering on positive plates.

Figure 9 shows the AID tree for predicting the presence of failure characteristic (L), high pressure, bulge, or convex sides. The most extreme frequency is associated with 12 cells, characterized as follows:

(U) present (high voltage on charge)
(T) present (short or open circuit)
(E) absent (separator not impregnated with negative plate material)
(I) absent (no blistering on positive plates)

Among these 12 cells, no cell showed high pressure, bulge, or convex sides.

Figure 10 shows the AID tree for predicting the presence of failure
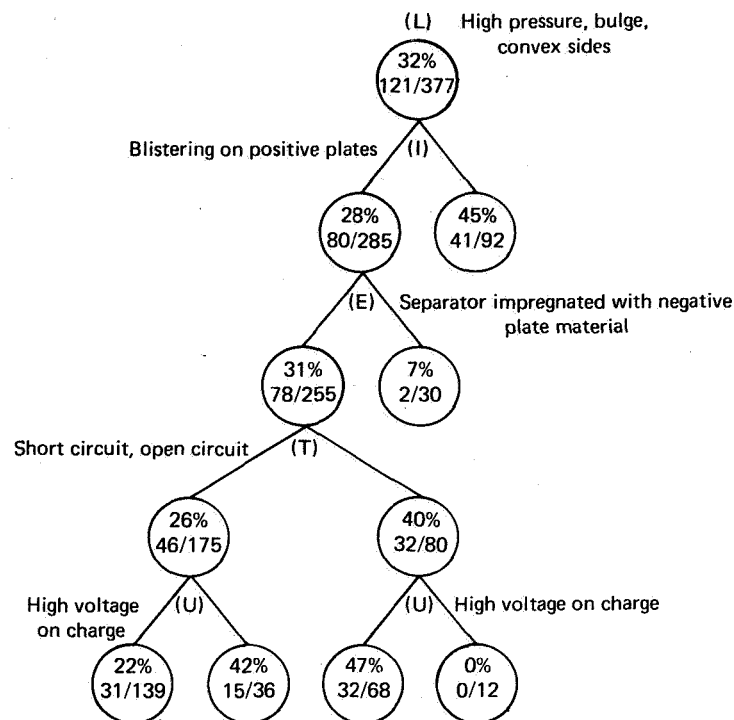
Figure 9—AID tree for predicting high pressure, bulge, or convex sides.

characteristic (O), ceramic shorts. One terminal node with low percentage involves 21 cells having the following characteristics:

(E) present (separator impregnated with negative plate material)
(B) present (low voltage on discharge)
(I) absent (no blistering on positive plates)
(T) absent (no short or open circuit)

Among these 21 cells, no cell had a ceramic short. Other terminal nodes with low percentages are seen to include those given by (B) absent, (I) absent, and (T) absent, and by (E) absent, (U) present, (I) present, and (T) absent.

Figure 11 shows the AID tree for predicting the presence of failure characteristic (T), short or open circuits. The tree shows one perfect split on characteristic (O), ceramic short, into 100- and 0-percentage nodes. After splitting on (B), (I), and (O), a set of 14 cells is defined by the following characteristics:

(O) absent (no ceramic short)
(I) present (blistering on positive plates)
(B) absent (no low voltage on discharge)
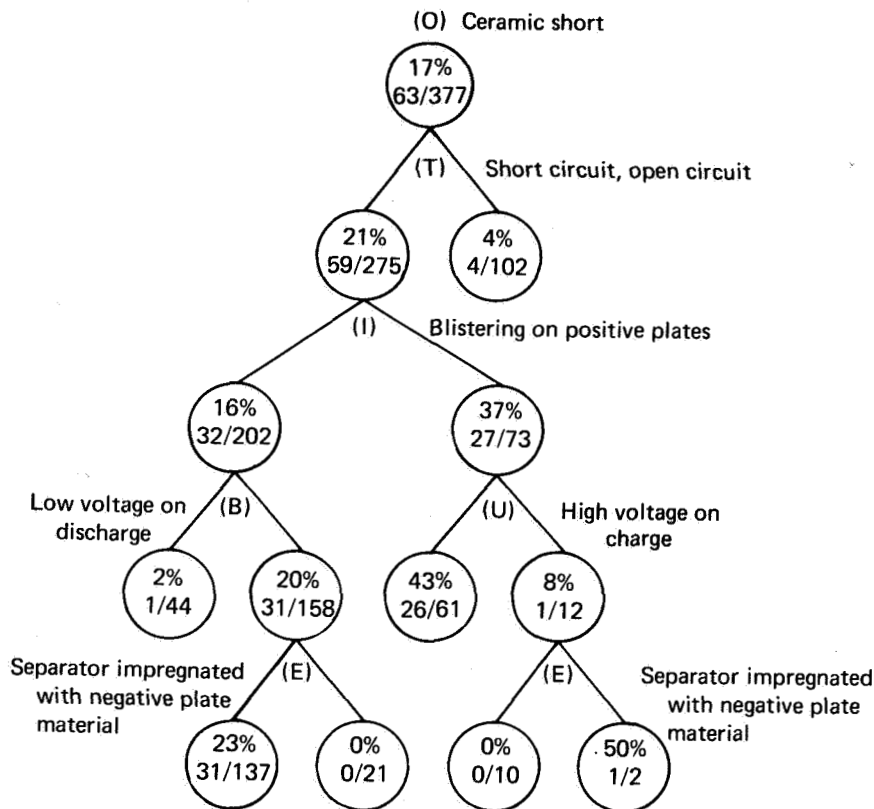
Figure 10—AID tree for predicting ceramic shorts.

For these 14 cells, each showed an open or short circuit. The other group formed by this split consisted of a single cell which showed a ceramic short, blistering on the positive plates, and no low voltage on discharge.

Figure 12 shows the AID tree for predicting the presence of failure characteristic (U), high voltage on charge. Only one failure characteristic yielded a split having a statistically significant F-ratio; this characteristic was low voltage on discharge. The tree shows that only 2 percent of the cells that had high voltage on charge also had low voltage on discharge.

In summary, it should be noted that the classifications yielded by the AID trees are generated by a computer; no understanding of the nature of the variables is required. It should not be surprising if some of the classifications have an evident physical meaning. It would be hoped that the classifications yielded by the computer program suggest additional classifications that may have been overlooked because of the large number of possible combinations of the variables. A simple calculation shows that, for the 21 variables listed in
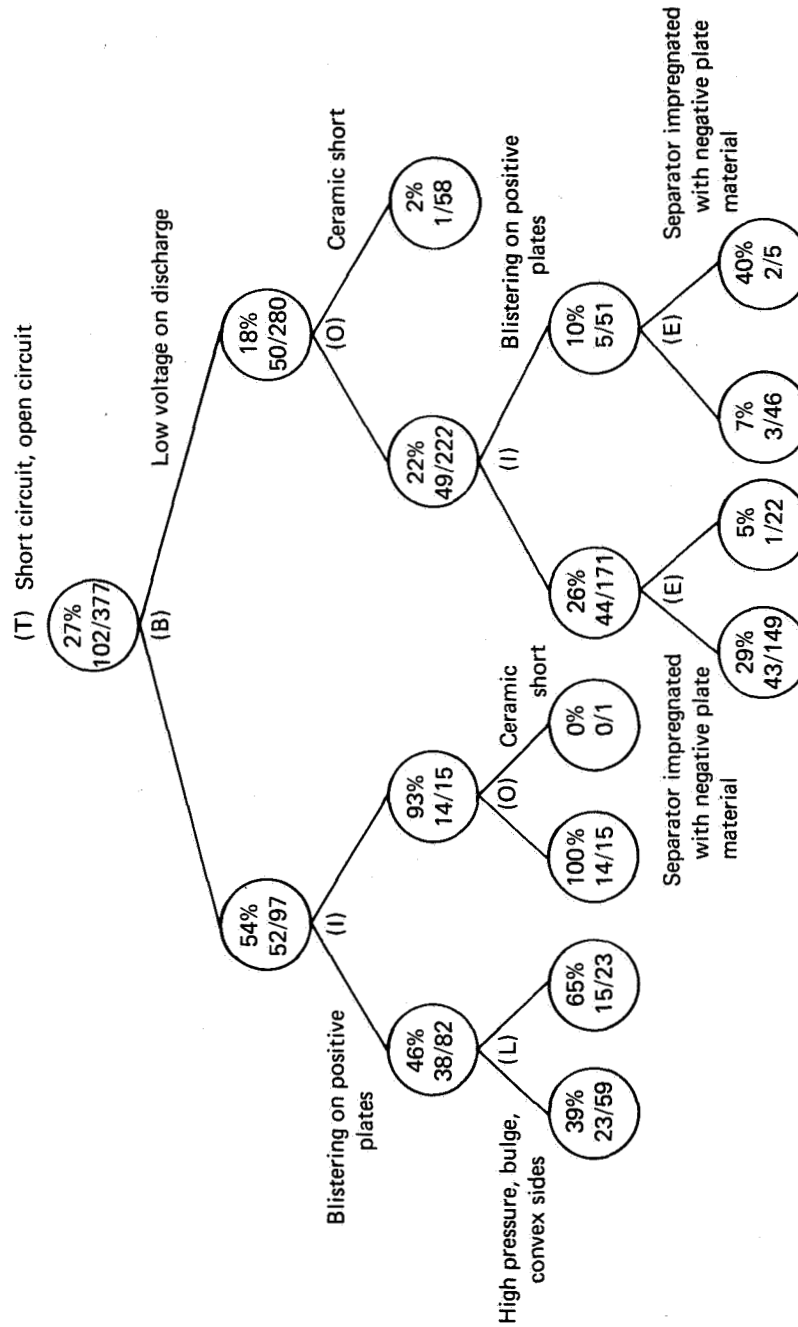
Figure 11–AID tree for predicting short or open circuits.
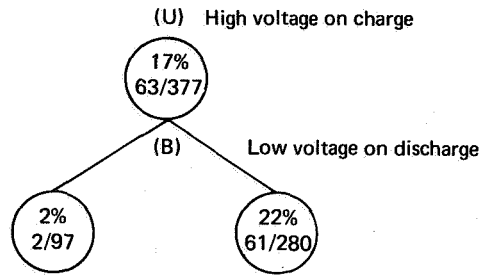
Figure 12–AID tree for predicting high voltage on charge.

Table 2, a total of over 2 million distinct combinations of failure characteristics is possible. A large portion of these combinations is actually evaluated by the computer program.

The Search for Embedded Statistical Designs

The purpose of an empirical analysis of data is to detect structure in the data. The preceding examples have shown how the AID program gives rise to tree structures. It is sometimes possible to find standard statistical designs embedded in empirically detected structures. Such statistical designs include both factorial and hierarchical designs. Consider, for example, the AID tree shown in Figure 9 for predicting high pressure, bulge, and convex sides. The subtree associated with the variables (T) and (U) can be analyzed as a 2 X 2 factorial experiment; this results from the fact that (T) occurs at two levels (present or absent) and (U) occurs at two levels for each level of (T). This symmetrical kind of split does not usually occur; for example, in the left branch of Figure 11, variable (L) is used to split the low level of (I), and a different variable, (O), is used to split the high level of (I).

The search for such embedded designs is useful because when such designs are found it is possible to assess the statistical significance of the structure from standard statistical methods. In Figure 9, for example, suppose that the number of cells having high pressures, bulges, or convex sides are analyzed using Yates' method (Reference 31). The data for this analysis may be obtained directly from the four lower nodes in the AID tree. (See also Table 4.) The coordinates in the left column of Table 4 show the combinations of levels associated with (T) and (U); that is, the coordinates (0, 0) indicate that both (T) and (U) are absent; (0, 1) indicates that (T) is absent and (U) is present; and so forth. N gives the number of cells found to be associated with the corresponding treatment combination. The main effects and interactions are as follows:

(1) The average number of cells involved in the four treatment combinations is 19.5.

Table 4—*Data from AID tree.*

(T), (U)	N
(0, 0)	31
(0, 1)	15
(1, 0)	32
(1, 1)	0

(2) The main effect of (U) is equal to -24. This means that the average number of cells showing high pressure, bulge, or convex sides is decreased by 24 when high voltage on charge is present relative to those cells in which high voltage on charge is absent.

(3) The main effect of (T) is equal to -7. This means that the average number of cells showing high pressure, bulge, or convex sides is decreased by 7 when short or open circuits are present relative to those cells when short or open circuits are absent.

(4) The interaction between (T) and (U) is equal to -8. Because this interaction is not zero, the effect of (U) depends on whether (T) is present and vice versa. That is, the effect of short or open circuits on the number of cells showing high pressure, bulges, or convex sides depends on whether high voltage on charge is present or absent.

This example serves to suggest the manner in which embedded statistical designs can be identified and analyzed in a standard statistical manner.

Assessing the Statistical Significance of the AID Tree

Because of the sequential manner in which the AID tree is developed, a theory does not exist on how to obtain an overall assessment of the statistical significance of a particular AID tree. As examples, statisticians would like to know if a similar set of cells, tested and analyzed using the AID program, would exhibit the same tree structure.

A statistical assessment of each individual split in an AID tree can be made from an analysis of variance. This analysis yields an F-ratio whose statistical significance can be judged. The entire tree then represents a set of F-ratios with one F-ratio for each split. However, an accepted method for combining the various "local" F-ratios to form a single "global" F-ratio is not available. As an approximation in obtaining a statistically significant AID tree, it is possible to apply an analysis of variance to each split in the AID tree and retain the split in subtrees only if the F-ratio is statistically significant. This procedure was followed in obtaining the preceding examples of AID trees.

At a global level, an approximate statistical assessment can be made in terms of the terminal nodes of a particular AID tree. For example, consider the AID tree for predicting high pressure, bulge, or convex sides in Figure 9. A standard

Table 5—*Analysis of variance.*

Source	Sum of Squared Deviations (SSD)	Degrees of Freedom	Mean Square	F-Ratio
Between terminal nodes	7.78	5	1.556	7.78
Within terminal nodes	74.38	371	0.200	—
Total	82.16	376	—	—

analysis of variance for the terminal nodes for this tree is given in Table 5. The F-ratio of 7.78 is statistically significant at the 5-percent level of significance. Thus, the AID tree associated with this analysis would be expected to be obtained again if a similar set of data were analyzed.

Analytic Formulations

Because of the importance of tree structures in empirical analyses, it becomes desirable to express a tree in algebraic form so that the equation of the tree then may be examined for algebraic structure. This analysis, in turn, may aid in the understanding of the physical mechanisms involved in the tree structure.

To show that such a procedure is possible, the following equation may be verified for the percentages given in the terminal nodes of the AID tree for predicting high pressure, bulge, or convex sides (Figure 9):

$$P = 22[1 - (U)] [1 - (T)] [1 - (E)] \frac{1 - (I)}{2^4}$$
$$+ 42[1 + (U)] [1 - (T)] [1 - (E)] \frac{1 - (I)}{2^4}$$
$$+ 47[1 - (U)] [1 + (T)] [1 - (E)] \frac{1 - (I)}{2^4}$$
$$+ 7[1 + (E)] \frac{1 - (I)}{2^2} + 45 \frac{1 + (I)}{2},$$

where P denotes the percentage of the cells showing high pressure, bulge, or convex sides in each terminal node. The variables (U), (T), (E), and (I) are set equal to 1 or -1, accordingly, as the associated failure characteristic is present or absent. For example, if (U), (T), (E), and (I) are all absent, then

(U) = (T) = (E) = (I) = -1 and all terms except the first are equal to zero, so that

$$P = (22)(2)(2)(2) \frac{2}{2^4} = 22 ,$$

as shown in the lower left-hand node in Figure 9. The remaining percentages in Figure 9 may be calculated similarly from this equation. The percentages are seen to occur as coefficients in the algebraic formulation.

This example shows that the AID tree can be mathematically represented in a form analogous to regression equations. However, in contrast to regression, the assumptions associated with an AID tree are minimal. Moreover, the algebraic structure is more suitable for physical interpretation than is the diagrammatic structure associated with an AID tree.

SUMMARY OF EMPIRICAL APPROACH

The preceding examples show that empirical methods are capable of extracting a considerable amount of data structure with the single prior assumption that the data can be identified. The generality of the AID tree structure is particularly attractive as an empirical tool to be used in the analysis of accelerated test data. Considerable information may be obtained from direct examination of such trees to determine the relative importance of predictive variables and the effects of various conditions along different branches of the tree. Still more information may be obtained through computations related to statistical reliability estimates, F-ratios, and embedded statistical designs. The algebraic expression of the tree gives still further insight into the mathematical relations among the variables. All of these observations show that empirical methods form a potentially powerful approach to data monitoring and analysis. The difficulties associated with the empirical approach stem largely from a lack of computer software.

The following list gives a summary of the data requirements for the empirical approach to the accelerated testing of rechargeable cells:

(1) Full identification of cells to be put on test, including manufacturer type, size, lot number, plate formation data, previous history, and so forth, to permit the association of pretest experience with observed behavior of the cell during the test

(2) Preliminary examination data, including results of acceptance testing, screening tests, tear-down tests, and so forth, to permit the possible association of the initial condition of the cell with observed behavior of the cell during the test

(3) Twelve cell-voltage measurements taken within each charge/discharge cycle, or measurements taken at 2-min intervals, whichever yields more data, to relate, through empirical methods such as the AID

program, degradation of quality to stress level, initial condition, and pretest experience of the cell.

The empirical approach requires full identification of the cells to be put on test, together with all data obtained from preliminary examinations, acceptance tests, and screening tests. Such data may be found to be closely related to observed cell behavior during the accelerated test. To provide adequate data for an empirical analysis, it is recommended that cell-voltage measurements be taken every 2 min within each charge/discharge cycle, with an additional requirement that at least 12 cell-voltage measurements be obtained in each cycle.

Because of the extensive data-analysis requirements of the empirical approach, an offline computer system is required. In addition, some online computer capability is required for minimal processing, including the tagging of certain output data for more efficient offline data processing. In an ideal test program, an online computer capability of 16 000 words is recommended. (See Section 6.)

4 STATISTICAL APPROACH

A response-surface analysis is developed in this section as a method that exemplifies a statistical approach to the analysis of accelerated test data. The response-surface analysis was selected because it appears to be well suited for making a transition between an empirical approach and a statistical approach. In the empirical approach, the response surface is fitted exactly to the observed data so that no smoothing or averaging of data is involved. Typically, the statistician objects to the exact fitting of a response surface because in such a case the surface is fitted to the combined signal and noise components of the data. The statistician prefers to assess the magnitude of the noise component of the data and then fit a smoothed response surface. In this case, the surface does not, in general, pass through the data points. Instead, the surface approaches the data points within a miss distance that is associated with the noise component or experimental error. To illustrate the selected method, the following paragraphs give an example in which both an exact fit (empirical) and a smoothed fit (statistical) are given for the same set of data. In addition, the coefficients obtained by this approach may be plotted as functions of time. The resulting response surface is then shifted to allow predictions to be made of future positions of the surface. In turn, these predictions can be interpreted in terms of predicted behavior of the cells on test. For these reasons, the selected approach is called a dynamic response-surface approach to the analysis of accelerated test data. The principal characteristics of this approach are summarized.

DYNAMIC RESPONSE-SURFACE APPROACH

Consider a response-surface approach that has the following properties:

(1) Measurements of cell quality are expressed as surface functions of the remaining variables at given instants of time.

(2) These surface functions may be constructed so that the resulting equations fit the measured values exactly, with the result that empirical analysis is not hampered by smoothing of the data.

(3) The same approach may be used to smooth the data and obtain results that are consistent with current statistical methods of analysis.

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(4) The coefficients of the fitted equations may be studied to determine their behavior over time and thereby aid in predictions of cell characteristics.

(5) The magnitudes of the coefficients, their associated time rates of change, and their relationships to various subsets of the variables may suggest physical mechanisms that are associated with degradations over time of the quality surface.

In brief, the technical approach involves the fitting of orthogonal polynomials to the data. Such an approach is described in References 32 to 34. To extend the customary approach to the context of accelerated testing, the mathematical method is described below. For purposes of exposition, data published by Albrecht (Reference 35) are used as a basis for developing the method. The extensions of the method to the case of measurement tables at successive times are described briefly.

Table 6 shows a portion of Albrecht's data; the reader is referred to Albrecht's paper (Reference 35) for a thorough discussion of these results. In the present development, these data are used as a convenient basis for illustrating the response-surface approach to data analysis.

In standard statistical terminology, Table 6 shows results for an experiment involving four factors. The temperature factor has two levels, corresponding to 244 K ($-20°$ F) and room temperature (RT); the charge duration factor has three levels, corresponding to 3, 7, and 10 days; the charging rate has two levels, corresponding to 7 or 14 mA of current; and the manufacturer has three levels, coded 2, 3, and 5, corresponding to the respective suppliers. Statistically, these data represent the results of a $3 \times 2 \times 2 \times 3$ factorial experiment having 36 treatment combinations, as shown by the 36 numbers given in Table 6. The objective of the following paragraphs consists of fitting a particular five-dimensional response surface to these data.

A Local Response Curve

Consider the results associated with manufacturer 2, a temperature of 244 K ($-20°$ F), and a charging current of 7 mA. The ampere-hour efficiencies are given by 95.9, 96.5, and 102.4 percent and correspond to charge durations of 3, 7, and 10 days, respectively. For simplicity, the charge durations are coded as -1, 0, and 1, as shown by the numbers in parentheses. This coding requires that the three charge durations be equally spaced; that is, the coding strictly requires a charge duration of 6.5 days instead of 7 days. This discrepancy is not important, however, for the development of the following procedure.

The response surface will be developed in several steps. In the first step, a quadratic equation is fitted to the data shown in the first three columns in table 7. The three columns appended to these data give the values of the three polynomials at the coded values of x. For example, the numbers in the last column are obtained by evaluating $P_2(x_1) = 3x_1^2 - 2$ at x_1 values of -1, 0, and

Table 6—*Average ampere-hour efficiency of nickel-cadmium batteries.*[a]

	Average Efficiency (percent)											
Manufacturer[b]	2 (-1)				3 (0)				5 (1)			
Temperature[c]	244 K (-20° F)(-1)		RT (1)		244 K (-20° F)(-1)		RT (1)		244 K (-20° F) (-1)		RT (1)	
Current (mA)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)	7 (-1)	14 (1)
Charge duration (days)												
3 (-1)	95.9	97.6	67.8	81.4	98.0	93.3	113.3	84.9	99.4	116.0	43.4	76.1
7 (0)	96.5	96.6	77.8	77.9	96.7	98.4	87.3	91.2	100.0	88.3	85.0	84.8
10 (1)	102.4	98.9	76.5	67.5	104.7	100.4	75.1	76.9	83.9	90.7	68.6	71.7

[a]Data obtained from Tables IV and V of Reference 35.
[b]Numbers in parentheses denote coded values.
[c]RT: room temperature.

Table 7—*Data for quadratic equation and values of polynomials for development of response surface.*

Charge Duration (days)	Coded Value, x_1	Ampere-Hour Efficiency, y	$P_0(x_1) = 1$	$P_1(x_1) = x_1$	$P_2(x_1) = 3x_1^2 - 2$
3	−1	95.9	1	−1	1
7	0	96.5	1	0	−2
10	1	102.4	1	1	1

1. It is also seen that these columns are mutually orthogonal. For example, the last two columns show that $(-1)(1) + (0)(-2) + (1)(1) = 0$. A similar result holds for any pair of the last three columns. As shown later, this property of orthogonality is of special importance in statistical analysis of the data.

By means of the four columns on the right of the preceding tabulation, the following determinant is then formed and set equal to zero:

$$\begin{vmatrix} \dfrac{y}{95.9} & \dfrac{1}{1} & \dfrac{x_1}{-1} & \dfrac{3x_1^2-2}{1} \\ 96.5 & 1 & 0 & -2 \\ 102.4 & 1 & 1 & 1 \end{vmatrix} = 0.$$

An expansion of this determinant gives a quadratic equation that is desired for relating ampere-hour efficiency y to duration of charge x_1. The expansion yields

$$6y - 589.6 - 19.5x_1 - 5.3(3x_1^2 - 2) = 0 . \tag{2}$$

Rewritten, Equation 2 yields

$$y(x_1) = 98.27 + 3.25x_1 + 0.88(3x_1^2 - 2) . \tag{3}$$

Substitution of $x_1 = -1$, 0, and 1 into Equation 3 yields $y(-1) = 95.9$, $y(0) = 96.5$, and $y(1) = 102.4$; thus, Equation 3 gives an exact fit to the original data points.

Interpretation of the Coefficients

The coefficients of Equation 3 may be interpreted as follows:

(1) The constant term 98.27 is the average ampere-hour efficiency over all three temperatures; i.e., $98.27 = (95.9 + 96.5 + 102.4)/3$.

(2) The change in ampere-hour efficiency between charge durations of 7 and 3 days is $96.5 - 95.9 = 0.6$. Similarly, the change in ampere-hour efficiency between the charge durations of 7 and 10 days is $102.4 - 96.5 = 5.9$. The average of these two changes is

$(0.6 + 5.9)/2 = 3.25$. This is seen to be the coefficient of x in the fitted equation. For this reason, the coefficient may be associated with the average linear effect of charge duration on ampere-hour efficiency.

(3) The coefficient of the x^2 term, 0.88, may be associated with the quadratic effect of charge time on ampere-hour efficiency.

These meanings of the coefficients will be retained in the extended surface-fitting procedures that follow.

Application of the same procedure to the second column of Table 6 yields a second response curve that relates ampere-hour efficiency to charge duration for batteries from manufacturer 2 at 244 K ($-20°$ F) with a charging current of 14 mA. The determinant is easily written by inspection:

$$\begin{array}{cccc} y & 1 & x_1 & 3x_1^2 - 2 \\ \hline \end{array}$$

$$\begin{vmatrix} 97.6 & 1 & -1 & 1 \\ 96.6 & 1 & 0 & -2 \\ 98.9 & 1 & 1 & 1 \end{vmatrix} = 0.$$

An expansion of this determinant yields the following equation:

$$y(x_1) = 97.70 + 0.65x_1 + 0.55(3x_1^2 - 2) . \tag{4}$$

This equation provides a second relation between ampere-hour efficiency and charge duration. The relation differs from that previously obtained by the fact that the associated data were taken at a charging rate of 14 instead of 7 mA. The differences in the corresponding coefficients of the two equations thus may be associated with the difference in charging current. To obtain a quantitative expression that brings charging current into the equation, it is necessary to combine these two response curves into a response surface. First, however, note that each of these equations simply replaces three measured values with three coefficients. In the above example, the measured ampere-hour efficiencies 97.6, 96.6, and 98.9 are replaced by the coefficients 97.7, 0.65, and 0.55. The value of these replacements lies in the fact that the coefficients have physical interpretations given by the average ampere-hour efficiency, the linear effect of charge duration of ampere-hour efficiency, and the nonlinear (quadratic) effect of charge duration on ampere-hour efficiency. Because the fit is exact, no information is lost in transforming the measured values into the coefficients. Because no smoothing takes place, an empirical analysis is not hindered. On the other hand, if smoothing is desired, it is easily accomplished, as will be shown in a later section.

Table 8 shows a listing of the coefficients obtained for each column of data appearing in Table 6. The first three columns of Table 8 give the coded values that correspond to those given in parentheses in Table 6. Columns 4, 5, and 6 give the coefficients A, B, and C of the response equation

$$y(x_1) = A + Bx_1 + C(3x_1^2 - 2) \tag{5}$$

Table 8—*Summary of coefficients for response curves based on charge duration.*[a]

Experimental Conditions			Average[b]	Linear Effect of Charge Duration[c]	Quadratic Effect of Charge Duration[d]
Manufacturer	Temperature	Current			
−1	−1	−1	98.27	3.25	0.88
−1	−1	1	97.70	0.65	0.55
−1	1	−1	74.03	4.35	−1.88
−1	1	1	75.60	−6.95	−1.15
0	−1	−1	99.80	3.35	1.55
0	−1	1	97.37	3.55	−0.52
0	1	−1	91.90	−19.10	2.30
0	1	1	84.33	−4.00	−3.43
1	−1	−1	94.43	−7.75	−2.78
1	−1	1	98.33	−12.65	5.02
1	1	−1	65.67	12.60	−9.67
1	1	1	77.53	−2.20	−3.63

[a]Based on data of Reference 35.
[b]Constant term in response equation.
[c]Coefficient of x_1 in Equation 5.
[d]Coefficient of $(3x_1^2 - 2)$ in Equation 5.

for each of the 12 rows. These equations will be further combined to represent the effects of charging current, temperature, and manufacturer.

Extending Response Curves to Response Surfaces

For the first two columns of Table 6, Equations 3 and 4 were obtained. These two equations give exact fits to Albrecht's data for manufacturer 2 and a temperature of 244 K ($-20°$ F). Equation 3 relates ampere-hour efficiency to charge duration at 7 mA; Equation 4 relates ampere-hour efficiency to charge duration at 14 mA. These two equations will be combined into a single equation that expresses ampere-hour efficiency y as a function of both charge duration x_1 and charge rate x_2.

To begin, note that the matrix of coefficients appended to the data to obtain the above equations is given by

$$M_3 = \begin{array}{ccc} P_0(x) & P_1(x) & P_2(x) \\ \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} \end{array},$$

where $P_0(x) = 1$, $P_1(x) = x$, and $P_2(x) = 3x^2 - 2$. This matrix of coefficients is a standard matrix and may be used for any factor that has three levels. In the

previous cases, for example, charge duration had three levels with coded values of -1, 0, and 1 corresponding to 3, 7, and 10 days. Because the order of the matrix must equal the number of levels of the factor being analyzed, it is necessary to have a 2 X 2 matrix for a factor with two levels, a 3 X 3 matrix for a factor with three levels, and so forth.

Table 9 shows the basic matrices for the orthogonal polynomials used in this development for factors having two through five levels. More extensive tables of such matrices may be found in several sources (References 32 and 36).

As shown in Table 9, the matrix associated with a factor having two levels is given by

$$\mathbf{M}_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}.$$

Because the charge current has two levels (7 and 14 mA) this matrix is to be associated with the analysis of charge current. To generate an equation that accounts for both charge duration and charge current, it is necessary to combine the $\mathbf{M}_2$ and $\mathbf{M}_3$ matrix. Symbolically, the matrix $\mathbf{M}$ may be written as

$$\mathbf{M} = \begin{bmatrix} \mathbf{M}_3 & -\mathbf{M}_3 \\ \mathbf{M}_3 & \mathbf{M}_3 \end{bmatrix},$$

so that it has $\mathbf{M}_3$ matrices as its elements and, further, that these $\mathbf{M}_3$ matrices are multiplied by the corresponding elements of the $\mathbf{M}_2$ matrix. Substitution of the numerical values yields

$$\mathbf{M} = \begin{bmatrix} 1 & -1 & 1 & \vdots & -1 & 1 & -1 \\ 1 & 0 & -2 & \vdots & -1 & 0 & 2 \\ 1 & 1 & 1 & \vdots & -1 & -1 & -1 \\ \cdots & \cdots & \cdots & \vdots & \cdots & \cdots & \cdots \\ 1 & -1 & 1 & \vdots & 1 & -1 & 1 \\ 1 & 0 & -2 & \vdots & 1 & 0 & -2 \\ 1 & 1 & 1 & \vdots & 1 & 1 & 1 \end{bmatrix},$$

and the determinant that yields the desired equation is

(x_2, x_1)	$y(x_1, x_2)$	1	x_1	$3x_1^2 - 2$	x_2	$x_1 x_2$	$(3x_1^2 - 2)x_2$
$(-1, -1)$	95.9	1	-1	1	-1	1	-1
$(-1, 0)$	96.5	1	0	-2	-1	0	2
$(-1, 1)$	102.4	1	1	1	-1	-1	-1
$(1, -1)$	97.6	1	-1	1	1	-1	1
$(1, 0)$	96.6	1	0	-2	1	0	-2
$(1, 1)$	98.9	1	1	1	1	1	1

$= 0.$

It is noted that charge rate x_2 has been coded so that $x_2 = -1$ when the charge rate is 7 mA and $x_2 = 1$ when the charge rate is 14 mA. The coded values corresponding to the treatment combinations are shown in the column at the left of the determinant; these correspond to the coded values shown in

Table 9—*Basic matrices for generation of response surfaces.*

Number of Levels of a Specified Factor	Basic Matrix
2	$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$
3	$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix}$
4	$M_4 = \begin{bmatrix} 1 & -3 & 1 & -1 \\ 1 & -1 & -1 & 3 \\ 1 & 1 & -1 & -3 \\ 1 & 3 & 1 & 1 \end{bmatrix}$
5	$M_5 = \begin{bmatrix} 1 & -2 & 2 & -1 & 1 \\ 1 & -1 & -1 & 2 & -4 \\ 1 & 0 & -2 & 0 & 6 \\ 1 & 1 & -1 & -2 & -4 \\ 1 & 2 & 2 & 1 & 1 \end{bmatrix}$

parentheses in Table 6. If the determinant is expanded using the elements of the first row, a polynomial of the following form will be obtained:

$$y(x_1, x_2) = A + Bx_1 + C(3x_1^2 - 2) + Dx_2 + Ex_1x_2 + F(3x_1^2 - 2)x_2, \quad (6)$$

where A, B, C, D, E, and F are coefficients.

For Albrecht's data, the expansion of the above determinant yields

$$y(x_1, x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2 - 2)$$

$$- 0.28x_2 - 1.30x_1x_2 - 0.17(3x_1^2 - 2)x_2. \quad (7)$$

This equation gives the ampere-hour efficiency $y(x_1, x_2)$ as a function of the coded values of charge duration x_1 and charge current x_2. Geometrically, the equation represents a response surface in three dimensions.

The interpretation of the coefficients obtained for this response surface is analogous to that given for the previous response curves:

A Average ampere-hour efficiency

B Linear effect of charge duration on ampere-hour efficiency

C Quadratic effect of charge duration on ampere-hour efficiency

D Linear effect of charge current on ampere-hour efficiency

E Linear-by-linear interaction between charge duration and charge current

F Quadratic-by-linear interaction between charge duration and charge current.

More detailed assessments of the above kinds of coefficients may be found in References 37 to 39. For the present, it is sufficient to note that the procedure described gives an exact fit to the data. Thus, for example, if Equation 7 is evaluated at the point corresponding to a charge duration of 3 days and a charge current of 14 mA, then $x_1 = -1, x_2 = 1$, and the ampere-hour efficiency is found to be $y(-1, 1) = 97.6$, as desired.

It should be emphasized that this calculation is made with the coded values shown in parentheses in Table 6. These coded values represent the coordinates of a point below the response surface. This kind of coding greatly simplifies the calculations. In the coding used in these examples, the lowest level of a factor is coded as -1 and the highest level is coded as $+1$. In this way, all points between -1 and 1 represent conditions within the range of the experimental conditions. The coded values of any condition within the extremes is obtainable by linear interpolation. For example, the coded value x corresponding to a specified level z of a factor that varies between z_{min} and z_{max} is given by

$$x = -1 + 2 \frac{z - z_{min}}{z_{max} - z_{min}} . \tag{8}$$

It is seen that when $z = z_{min}$, coded value x is equal to -1; and when $z = z_{max}$, the coded value x is equal to $+1$. In the above example, the minimum and maximum values of charge duration are given by 3 and 10 days, respectively; therefore,

$$x_1 = -1 + 2 \frac{z_1 - 3}{10 - 3}$$

$$= \frac{2z_1 - 13}{7} .$$

Similarly, the maximum and minimum values of charging current are 7 and 14 mA; hence,

$$x_2 = -1 + 2 \frac{z_2 - 7}{14 - 7}$$

$$= \frac{2z_2 - 21}{7} .$$

With these expressions, the coded values corresponding to 4 days and 12 mA are given by

$$x_1 = \frac{8 - 13}{7}$$

$$= -5/7$$

and

$$x_2 = \frac{24 - 21}{7}$$

$$= 3/7 .$$

An interpolated value for the ampere-hour efficiency may be obtained for these conditions by substitution in the response-surface equation:

$$y(-5/7, 3/7) = 97.98 + 1.95(-5/7) + 0.72[3(-5.7)^2 - 2]$$

$$- 0.28(3/7) - 1.30(-5/7)(3/7) - 0.17[3(5/7)^2 - 2](3/7)$$

$$= 96.56 .$$

Similar interpolations may be made for other conditions of interest.

Extending the Response Surface to Higher Dimensions

As shown by the preceding development, three dimensions are required to represent data involving two factors (one dimension for each factor and one dimension for the dependent variable). In general, a space of $n + 1$ dimensions is required for n factors. Thus, for all of the data shown in Table 6, a five-dimensional space is required. The algebraic development of the required response surface is simple and requires merely a continuation of the approach developed thus far. For example, to represent the data shown in Table 6, an orthogonal matrix of order 36 must be generated because there are 36 numbers to be represented. The first factor is charge duration x_1; because this factor has three levels, the associated basic matrix is given by

$$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} .$$

The second factor is charging current x_2 at two levels, with an associated basic matrix given by

$$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} ;$$

the third factor is temperature x_3 at two levels, with a basic matrix given by

$$M_2 = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} ;$$

and the fourth factor is manufacturer x_4 at three levels, with a basic matrix given by

$$M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} .$$

These matrices are sequentially combined as follows. As before, a new matrix is formed from M_1 and M_2 to obtain an intermediate matrix, M^{**}:

$$M^{**} = \begin{bmatrix} (1)M_3 & (-1)M_3 \\ (1)M_3 & (1)M_3 \end{bmatrix} .$$

In the same manner, the next matrix, M^{***}, is expressed in terms of M^{**} as follows:

$$M^{***} = \begin{bmatrix} (1)M^{**} & (-1)M^{**} \\ (1)M^{**} & (1)M^{**} \end{bmatrix} .$$

The final matrix is given by

$$M^{****} = \begin{bmatrix} (1)M^{***} & (-1)M^{***} & (1)M^{***} \\ (1)M^{***} & (0)M^{***} & (-2)M^{***} \\ (1)M^{***} & (1)M^{***} & (1)M^{***} \end{bmatrix}$$

It is seen that the procedure may be described as follows. Consider a matrix M that has been generated for the first n factors. Suppose that the next factor to be included in the representation has k levels, with a basic matrix denoted by M_k. The next matrix required, then, to represent the $n + 1$ factor is obtained from M_k by replacing each element of M_k with the product of the matrix M and the original element of M_k.

In the present example, it is found that

$$M^* = M_3 = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & -2 \\ 1 & 1 & 1 \end{bmatrix} .$$

Hence, as before,

$$M^{**} = \left[\begin{array}{rrr:rrr} 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 0 & -2 & -1 & 0 & 2 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ \hdashline 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & 0 & -2 & 1 & 0 & -2 \\ 1 & 1 & 1 & 1 & 1 & 1 \end{array}\right]$$

and

$$M^{***} = \left[\begin{array}{rrrrrr:rrrrrr} 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 \\ 1 & 0 & -2 & -1 & 0 & 2 & -1 & 0 & 2 & 1 & 0 & -2 \\ 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\ 1 & 0 & -2 & 1 & 0 & -2 & -1 & 0 & 2 & -1 & 0 & 2 \\ 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 \\ \hdashline 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 0 & -2 & -1 & 0 & 2 & 1 & 0 & -2 & -1 & 0 & 2 \\ 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & 0 & -2 & 1 & 0 & -2 & 1 & 0 & -2 & 1 & 0 & -2 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{array}\right]$$

The matrix **M***** is capable of generating an equation that accounts for the dependence of ampere-hour efficiency on charge duration, charge current, and temperature. A separate equation is generated for each manufacturer. These three equations may then be combined by means of **M******. However, because the arguments are analogous for any of these representations, it is more convenient to consider **M***** in more detail and present only the results obtained for **M******.

The determinantal equation that arises from **M***** for manufacturer 2 is

y	1	x_1	$(3x_1^2-2)$	x_2	x_1x_2	$(3x_1^2-2)x_2$	x_3	x_1x_3	$(3x_1^2-2)x_3$	x_2x_3	$x_1x_2x_3$	$(3x_1^2-2)x_2x_3$
95.9	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
96.5	1	0	-2	-1	0	2	-1	0	2	1	0	-2
102.4	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
97.6	1	-1	1	1	-1	1	-1	1	-1	-1	1	-1
96.6	1	0	-2	1	0	-2	-1	0	2	-1	0	2
98.9	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
67.8	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
77.8	1	0	-2	-1	0	2	1	0	-2	-1	0	2
76.5	1	1	1	-1	-1.	-1	1	1	1	-1	-1	-1
81.4	1	-1	1	1	-1	1	1	-1	1	1	-1	1
77.9	1	0	-2	1	0.	-2	1	0	-2	1	0	-2
67.5	1	1	1	1	1	1	1	1	1	1	1	1

$= 0.$

The expansion of this expression yields the following equation:

$$y(x_1, x_2, x_3) = 93.35 - 4.05x_1 - 0.025(3x_1^2 - 2) - 2.50x_2$$

$$+ 3.825x_1x_2 - 1.95(3x_1^2 - 2)x_2 - 5.23x_3 - 7.50x_1x_3$$

$$- 5.42(3x_1^2 - 2)x_3 - 1.283x_2x_3 + 3.725x_1x_2x_3$$

$$- 0.917(3x_1^2 - 2)x_2x_3 .$$

Similar equations may be obtained for the other two manufacturers.

Table 10 provides a listing of terms of the five-dimensional response surface that represents all of the data given in Table 6. Column 1 gives the conventional statistical labels associated with the various terms of the polynomial expansion. Column 2 gives the algebraic form of the terms appearing in the response equation; the last column gives the computed coefficients of these terms. The computations were made with a Fortran program written to compute the response coefficients for as many as five factors with as many as five levels per factor.

Exploration of the Response Surface

Once a set of data has been represented by a response surface, a wide variety of questions can be answered by examining properties of the surface. The meaning of the answers will depend on the meaning of the data. For Albrecht's data, for example, it may be meaningful to interpolate within the range of the experimental conditions for charge duration, charge current, and temperature because these variables are continuous. However, interpolation between

Table 10—*Summary of coefficients for response surface based on charge duration, charge current, temperature, and manufacturer.*[a]

Effects and Interactions	Term	Coefficient
Average	1	87.91
Linear effects:		
Charge duration D	x_1	−2.08
Charge current C	x_2	0.56
Temperature T	x_3	−9.74
Manufacturer M	x_4	−1.20
Linear-by-linear interactions:		
$D \times C$	$x_1 x_2$	−1.53
$D \times T$	$x_1 x_3$	−0.48
$D \times M$	$x_1 x_4$	−1.41
$C \times T$	$x_2 x_3$	0.41
$C \times M$	$x_2 x_4$	1.85
$T \times M$	$x_3 x_4$	−0.40
Linear-by-linear-by-linear interactions:		
$D \times C \times T$	$x_1 x_2 x_3$	−0.31
$D \times C \times M$	$x_1 x_2 x_4$	−0.73
$D \times T \times M$	$x_1 x_3 x_4$	4.66
$C \times T \times M$	$x_2 x_3 x_4$	0.73
Quadratic effects:		
D^2	$3x_1^2 - 2$	−1.06
M^2	$3x_4^2 - 2$	−2.72
Quadratic-by-linear interactions:		
$D^2 \times C$	$(3x_1^2 - 2)x_2$	0.54
$D^2 \times T$	$(3x_1^2 - 2)x_3$	−1.85
$D^2 \times M$	$(3x_1^2 - 2)x_4$	−1.18
$D \times M^2$	$x_1(3x_4^2 - 2)$	0.99
$C \times M^2$	$x_2(3x_4^2 - 2)$	1.53
$T \times M^2$	$x_3(3x_4^2 - 2)$	−2.25
Quadratic-by-quadratic interaction: $D^2 \times M^2$	$(3x_1^2 - 2)(3x_4^2 - 2)$	−0.52
Linear-by-linear-by-quadratic interactions:		
$D \times C \times M^2$	$x_1 x_2(3x_4^2 - 2)$	−2.68
$D \times T \times M^2$	$x_1 x_3(3x_4^2 - 2)$	3.51
$C \times T \times M^2$	$x_2 x_3(3x_4^2 - 2)$	0.85
$D^2 \times C \times T$	$(3x_1^2 - 2)x_2 x_3$	−0.36
$D^2 \times C \times M$	$(3x_1^2 - 2)x_2 x_4$	1.68
$D^2 \times T \times M$	$(3x_1^2 - 2)x_3 x_4$	−1.38
Linear-by-linear-by-linear-by-linear interaction: $D \times C \times T \times M$	$x_1 x_2 x_3 x_4$	−0.15

Table 10—*Concluded.*

Effects and Interactions	Term	Coefficient
Linear-by-linear-by-linear-by- quadratic interactions:		
$D^2 \times C \times T \times M$	$(3x_1^2 - 2)x_2 x_3 x_4$	−0.35
$D \times C \times T \times M^2$	$x_1 x_2 x_3 (3x_4^2 - 2)$	−2.02
Quadratic-by-quadratic-by-linear interactions:		
$D^2 \times C \times M^2$	$(3x_1^2 - 2)x_2 (3x_4^2 - 2)$	1.24
$D^2 \times T \times M^2$	$(3x_1^2 - 2)x_3 (3x_4^2 - 2)$	−0.65
Quadratic-by-quadratic-by-linear- by-linear interaction:		
$D^2 \times C \times T \times M^2$	$(3x_1^2 - 2)x_2 x_3 (3x_4^2 - 2)$	0.28

[a]Based on data of Reference 35.

manufacturers is not meaningful because the manufacturer is a discrete (nominal) variable. In general, interpolation of a given variable is expected to be meaningful if the variable is continuous; it is not expected to be meaningful if the variable is discrete.

Most properties of surfaces can be extracted from their equations by locating maxima and minima and finding directional derivatives, gradients, radii of curvature, and tangent planes. These properties may all be determined if the surface is represented by an equation that can be differentiated. The response surface generated by orthogonal polynomials allows easy differentiation; hence, surface properties are easily deduced. Because such mathematical investigations are standard calculus procedures, they are not examined in any detail in this report. However, in order to emphasize the practical results obtainable from these surface properties, it is noted that for Albrecht's data questions of the following kinds could be examined:

(1) Within the range of the experiment, what conditions would be expected to yield the maximum ampere-hour efficiency for the cells obtained from manufacturer 3?

(2) What combinations of charge durations and charge rates would be expected to yield an ampere-hour efficiency of 98 percent for the cells obtained from manufacturer 2?

(3) Given operating conditions at a charge duration of 7 days, a charge current of 10 mA, and a temperature of 273 K (32° F) for the cells of manufacturer 5, what combined change in temperature and charge rate would be expected to yield the maximum increase in ampere-hour efficiency?

Most of these questions require interpolation within the experimental points. It should be emphasized that it is not asserted that either interpolations or extrapolations would yield good results. In general, the validity of each case would require special examination. For the proposed application, the primary virtue of the fitted response surface does not lie in obtaining answers to these kinds of questions. Instead, the virtue lies in the fact that the coefficients of these polynomials yield a perfect fit at the data points, and no interesting structure is lost by smoothing. Moreover, as indicated above, the coefficients have physically meaningful interpretations. Further, the behavior of the coefficients may be monitored over time to obtain time rates of change of the surface properties. These changes may be useful indicators of the underlying changes in physical processes over time. Consequently, these changes would be expected to be useful in establishing degradation rates as functions of stress in accelerated tests.

Representation of Quality as a Dynamic-Response Surface

It has been shown how a response surface may be fitted to a set of data involving several factors and several levels for each factor. To apply this approach to an ideal accelerated test, it is proposed that the dependent variables be those of quality, as defined in Section 2. Thus, a response surface would be generated to represent the quality of the cells on test at various time intervals.

In symbolic terms, let $Q(x_1, \ldots, x_n, t)$ denote the quality response surface at time t. This symbolism shows that the quality is assumed to be expressible in terms of n factors $x_1, \ldots, x_n$. The number of levels for each factor is not shown by the symbol. The use of orthogonal polynomials will yield a polynomial surface. In contrast to the case exemplified with Albrecht's data, the coefficients are regarded as time dependent. By computing the coefficients periodically and making plots of their values as a function of time, it would be possible to monitor the dynamic structure of the quality surface over time. More specifically, it is proposed that extrapolations be made of these coefficient trajectories in order to estimate their magnitudes at future measurement times. In this way, a predicted response surface would be generated prior to taking the measurements. By comparing the predicted response surface with the actual response surface, considerable experience would be gained that would aid in obtaining answers to the following types of questions:

(1) How far into the future can reasonably good forecasts of the quality response surface be made?

(2) Are data being taken too frequently or too infrequently for forecasting purposes?

(3) Is the degradation of quality occurring more rapidly under certain conditions? (Should data be taken more frequently under these conditions?)

Graphical Interpretations

As outlined in previous reports, it is assumed that quality degrades over time and that the rate of degradation of quality is increased by increasing the stress. Clearly, satisfactory definitions for quality and stress are needed to use this conceptual framework, and it appears that useful definitions of quality are available. However, the problem of obtaining useful definitions of stress is much greater and is discussed in the physical approach to accelerated testing in Section 5.

An empirical approach toward defining stress consists of fitting a dynamic-response surface to the accelerated test data and then determining, for example, which portions of the surface are decreasing most rapidly over time. Presumably, the treatment combinations under these portions of the surface provide the most stress.

Figure 13 shows a sketch of these ideas in the form of a dynamic-response surface. The vertical axis represents the measured quality. The $x_1 x_n$-plane represents the n-dimensional space associated with the n factors. The two surfaces denote the response surfaces at two successive times. The upper surface shows a gradient vector that is a linear combination of the n factors that can be associated with the greatest expected increase of quality obtainable by choosing appropriate linear combinations of the factors. In general, this space derivative exists at each point of a given response surface and is obtained by partial differentiation of the quality response surface with respect to $x_1, \ldots, x_n$. The lower surface represents a quality response surface at a later
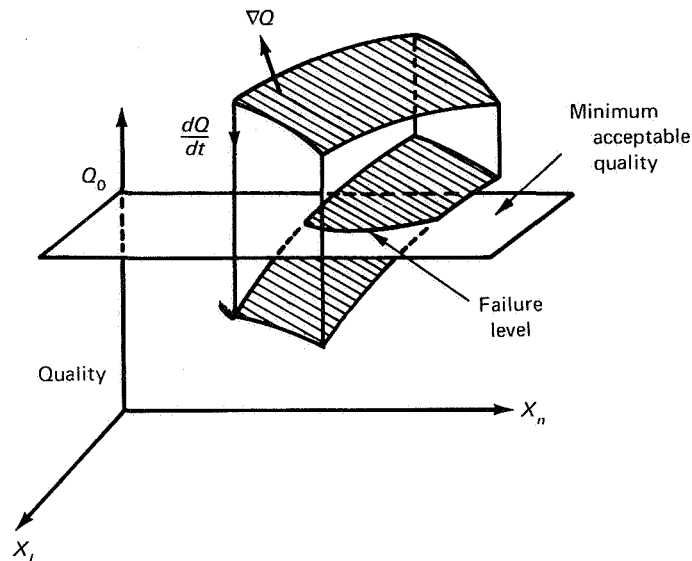

Figure 13—Dynamic response surface showing the degradation of quality.

time. The figure suggests a larger decrease of quality for the left portion of the surface. This is suggested by the vector labeled dQ/dt. The magnitude of this vector involves the time rates of change of the coefficients of the polynomials used to represent the response surface. The figure also shows a contour labeled "failure level." This boundary is associated with those conditions that give a minimal acceptable value of quality Q_0. The boundary results from a cross section of the lower response surface obtained with a plane parallel to the $x_1 x_n$-space. The equation of this boundary is obtained by setting $Q = Q_0$ in the response-surface equation.

Figure 14 shows the kinds of plots that may be used to monitor the coefficients of the fitted response surface. The dashed lines and the triangular symbols represent predicted values of the coefficients. Substitution of these predicted values into the response-surface equation will yield a predicted response surface. The six plots are hypothetical and are expressed in terms of average quality, together with the various linear and quadratic effects that would arise from three levels of charge duration and two levels of charge
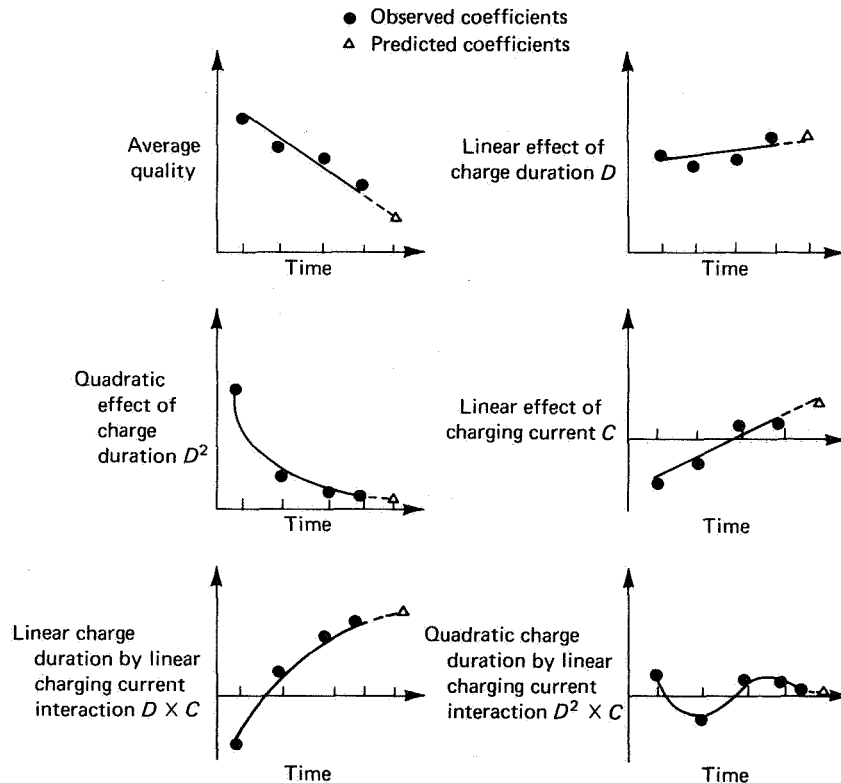

Figure 14—Hypothetical plots illustrating the prediction of the response-surface coefficients as a function of test time.

current. A total of 36 plots would be required to forecast the response surface for the kind of data presented in Table 6. Various methods are available for fitting and extrapolating such curves with computer software; but such methods will not be considered in detail in this report.

Statistical Smoothing of the Response Surface

The previous arguments focus attention on the fact that the response surfaces fit the data exactly at each data point. Statistical considerations generally involve the assumption that each data point consists of two components: signal and noise. In general, the purpose of statistical methods is to identify and assess the magnitudes of these two components. By fitting a response surface so that it passes exactly through the data points, the surface is fitted to the noise component as well as to the signal component. If the data are quite noisy, the usefulness of the response surface becomes questionable. Ideally, the statistician would smooth out the noise component and fit a response surface to the remaining signal component.

In many instances, identification of the noise contribution at each data point is difficult, if not impossible. Consequently, several procedures have evolved which are assumed to be useful. One of these methods involves fitting a response surface exactly, as described earlier, and omitting the higher degree terms from the polynomial equation. For example, if only the first-degree terms are retained, the resulting response surface is the customary hyperplane of linear regression analysis. On the other hand, if some of the coefficients of higher degree terms are large, it would be expected that these terms should be retained in the smoothed response surface because the dropping of these terms would be likely to produce large discrepancies between the data points and the response surface. A standard statistical method exists for determining which terms of the exact response surface should be retained; the method is illustrated here with a portion of Albrecht's data.

As shown earlier, the data of the first two columns of Table 6 are fitted exactly by the following response surface (Equation 7):

$$y(x_1, x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2 - 2) - 0.28x_2$$

$$- 1.30x_1x_2 - 0.17(3x_1^2 - 2)x_2 \,,$$

where x_1 denotes the coded value of charge duration and x_2 denotes the coded value of charging current. As a consequence of the orthogonality of the fitted polynomials, it may be shown that the total variance among the y values can be partitioned into six components. Each term in the response equation accounts for one of these components. In general terms, the total scatter of the data is measured in terms of the variance. This scatter is partitioned into six components; the statistical problem consists of determining which of the six components are noise and which are signal.

The portion of the total scatter associated with each term is easily obtained from the determinantal equation used to compute the response surface. As shown earlier, the following determinant may be written for the present example:

$$
\begin{array}{ccccccc}
y(x_1, x_2) & 1 & x_1 & (3x_1^2 - 2) & x_2 & x_1 x_2 & (3x_1^2 - 2)x_2 \\
\hline
95.9 & 1 & -1 & 1 & -1 & 1 & -1 \\
96.5 & 1 & 0 & -2 & -1 & 0 & 2 \\
102.4 & 1 & 1 & 1 & -1 & -1 & -1 \\
97.6 & 1 & -1 & 1 & 1 & -1 & 1 \\
96.6 & 1 & 0 & -2 & 1 & 0 & -2 \\
98.9 & 1 & 1 & 1 & 1 & 1 & 1
\end{array} = 0.
$$

The component of variance associated with the $1.95x_1$ term of the response-surface equation is computed as

$$ SSD = (1.95) \, [(95.9)(-1) + (102.4)(1) + (97.6)(-1) + (98.9)(1)] \, , $$

where the bracketed factor is obtained by taking the scalar product of columns 1 and 3 of the above determinant. The symbol SSD denotes the sum of squared deviations for x_1. Thus, it is found that $SSD_{x_1} = (1.95)(7.8) = 15.21$. In a similar way, the sum of squares associated with the $0.72(3x_1^2 - 2)$ term is found from columns 1 and 4 to be given by $SSD(3x_1^2 - 2) = (0.72)(8.6) = 6.192$. Continuing in this manner and summarizing the results yields the data given in Table 11. It is noted that the SSD associated with the constant (average) of the response equation is not shown, because the tabulation is intended to partition the variations about this average value. The third column gives the degrees of freedom. In general, there is one degree of freedom associated with each coefficient of the response equation. The five degrees of freedom in Table 11 plus one degree of freedom for the constant term give six degrees of freedom corresponding to the six data points fitted by the response surface.

Table 11—*Analysis of variance.*

Source of Variance	SSD	Degrees of Freedom df
Linear effect of charge duration D	15.210	1
Quadratic effect of charge duration D^2	6.192	1
Linear effect of charge current C	0.476	1
Linear-by-linear interaction $D \times C$	6.760	1
Quadratic-by-linear interaction $D^2 \times C$	0.340	1
Total	28.978	5

To assess the statistical significance of the magnitudes of the SSD's, a measure of the magnitude of the noise is needed. If the six data points are averages, the scatter within these averages is often used as a measure of the noise. For example, if each of six data points is based on an average of five cells, and if the SSD associated with these averages is equal to 12.00, the statistical analysis would take the form given in Table 12. The 24 degrees of freedom associated with the experimental error are obtained from the product of the number of means times four degrees of freedom per mean. The mean-square column is obtained by dividing the SSD's by the corresponding number of degrees of freedom. The F-ratios are formed by dividing each of the mean squares by the mean square for experimental error.

If it is assumed that the deviations about the means are normally distributed, the mean squares have χ^2-distributions, and the F-ratios have F-distributions (Reference 40). Large F-ratios indicate a large signal relative to the noise measured as the experimental error. In customary analyses, a large F-ratio is often taken to be a value that exceeds the noise level by an amount so large that the probability that it is not associated with a signal is less than 0.05. In these terms, the threshold F-ratio for Table 12 is found to be 4.26, corresponding to the 95-percent fractile of the F-distribution with one and 24 degrees of freedom. Those F-ratios larger than 4.26 are declared to be statistically significant. Table 12, the linear effect of charge duration, the quadratic effect of charge duration, and charge current are statistically significant. The linear effect of charge current and the quadratic-by-linear interaction $D^2 \times C$ are not statistically significant.

Because the effects associated with the x_2 term and the $(3x_1^2 - 2)x_2$ term of the response surface are not statistically significant, these terms would be dropped from the response-surface equation. Thus, for the above example, the smoothed response surface has the following equation:

$$\hat{y}(x_1, x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2 - 2) - 1.30x_1x_2 .$$

The surface represented by this equation will not pass through the data points exactly, presumably because the noise has been smoothed out. Table 13 shows

Table 12—*Statistical analysis of variance.*

Source of Variance	SSD	df	Mean Square	F-Ratio
Linear effect of charge duration D	15.210	1	15.210	30.42
Quadratic effect of charge duration D^2	6.192	1	6.192	12.38
Linear effect of charge current C	0.476	1	0.476	0.95
Linear-by-linear interaction $D \times C$	6.760	1	6.760	13.52
Quadratic-by-linear interaction $D^2 \times C$	0.340	1	0.340	0.68
Experimental error	12.000	24	0.500	—
Total	40.978	29	—	—

Table 13—*Comparison of actual data points with those of the smoothed response surface.*

Data Point, (x_2, x_1)	Actual Value, $y(x_1, x_2)$	Smooth Value, $\hat{y}(x_1, x_2)$	Difference, $\hat{y} - y$	$(\hat{y} - y)^2$
(-1, -1)	95.9	95.45	-0.45	0.2025
(-1, 0)	96.5	96.54	0.04	0.0016
(-1, 1)	102.4	101.95	-0.45	0.2025
(1, -1)	97.6	98.05	0.45	0.2025
(1, 0)	96.6	96.54	-0.06	0.0036
(1, 1)	98.9	99.35	0.45	0.2025
Total	—	—	—	0.8152

a comparison of the actual points and the values given by the smoothed response surface. The last column shows the square of the differences between the actual ampere-hour efficiencies and the smoothed values. The sum of the squared differences is equal to 0.8152. Within rounding errors, this sum is equal to the sum of the SSD's associated with the deleted terms. That is, the SSD for charging current in the above analysis-of-variance tabulation is seen to be 0.476, and the SSD for $D^2 \times C$ is seen to be 0.340. The sum of these SSD's is 0.816, which is approximately equal to 0.8152. Thus, the sum of the squares of the differences between the actual and smoothed data give the same measure of the noise that was associated with noise in the analysis-of-variance tabulation.

Interpretation of the Response Surface

The preceding development has shown how measured data can be represented by a response surface. For simplicity of exposition, the response surface has been generated as a linear combination of orthogonal polynomials. Such a representation appears artificial and, in general, would not be expected to yield equations that may be recognized as equations of physical processes. The variables of most physical equations can be represented as dimensionless variables, with functional relations involving exponential powers and products occurring more frequently than linear combinations. Linear combinations appear to arise most frequently in Taylor series approximations to the true functional relation. However, when the true functional relation is not known, the derivatives required for a Taylor series expansion cannot be taken. In such a case, it may be asked whether it is possible to estimate the derivatives from data and attempt to deduce the functional relation that would give rise to the empirically derived Taylor series. It will be shown that such an approach is convenient when the data are represented as a response surface of the form developed earlier.

Consider the response surface (Equation 7) derived for the first two columns of Table 6:

$$y(x_1, x_2) = 97.98 + 1.95x_1 + 0.72(3x_1^2 - 2)$$

$$- 0.28x_2 - 1.30x_1x_2 - 0.17(3x_1^2 - 2)x_2 .$$

The nonzero partial derivatives of this response surface are—

$$\frac{\partial y}{\partial x_1} = 1.95 + 4.32x_1 - 1.30x_2 - 1.02x_1x_2 ,$$

$$\frac{\partial y}{\partial x_2} = -0.28 - 1.30x_1 - 0.17(3x_1^2 - 2) ,$$

$$\frac{\partial^2 y}{\partial x_1^2} = 4.32 - 1.02x_2 ,$$

$$\frac{\partial^2 y}{\partial x_1 \partial x_2} = -1.30 - 1.02x_1 ,$$

and

$$\frac{\partial^3 y}{\partial x_1^2 \partial x_2} = -1.02 .$$

These derivatives are evaluated at the point $(\bar{x}_1, \bar{x}_2)$, where $\bar{x}_1$ and $\bar{x}_2$ denote the mean values of x_1 and x_2, respectively. Because x_1 has been coded to have values -1, 0, 1, the mean value is seen to be equal to 0. Similarly, because $x_2 = -1$, 1, the mean value of x_2 is equal to 0. Thus, the evaluation of the partial of y with respect to x_1 at $(\bar{x}_1, \bar{x}_2)$ is given by

$$\left(\frac{\partial y}{\partial x_1}\right)_{(\bar{x}_1, \bar{x}_2)} = \frac{\partial y}{\partial \bar{x}_1}$$

$$= 1.95 .$$

Similarly, the remaining partial derivatives evaluated at $(\bar{x}_1, \bar{x}_2)$ are obtained from the preceding expressions.

Next, suppose that the true, but unknown, functional equation for the response surface has a Taylor series expansion about the point (x_1, x_2), and let

$$f(x_1, x_2) = f(\bar{x}_1, \bar{x}_2) + \frac{\partial f}{\partial \bar{x}_1}(x_1 - \bar{x}_1) + \frac{\partial f}{\partial \bar{x}_2}(x_2 - \bar{x}_2)$$

$$+ \frac{1}{2}\left[\frac{\partial^2 f}{\partial x_1^2}(x_1 - \bar{x}_1)^2 + 2\frac{\partial^2 f}{\partial \bar{x}_1 \partial \bar{x}_2}(x_1 - \bar{x}_1)(x_2 - \bar{x}_2) + \frac{\partial^2 f}{\partial \bar{x}_2^2}(x_2 - \bar{x}_2)^2\right]$$

$$+ \frac{1}{6}\left[\frac{\partial^3 f}{\partial \bar{x}_1^3}(x_1 - \bar{x}_1)^3 + 3\frac{\partial^3 f}{\partial \bar{x}_1^2 \partial \bar{x}_2}(x_1 - \bar{x}_1)^2(x_2 - \bar{x}_2)\right.$$

$$\left. + 3\frac{\partial^3 f}{\partial \bar{x}_1 \partial \bar{x}_2^2}(x_1 - \bar{x}_1)(x_2 - \bar{x}_2)^2 + \frac{\partial^3 f}{\partial \bar{x}_2^3}(x_2 - \bar{x}_2)^3\right]$$

denote such an expansion through third partial derivatives. If this function is to represent the same data that were fitted by means of the orthogonal polynomials, it seems reasonable to set $\bar{x}_1 = \bar{x}_2 = 0$ and equate the values of the partial derivatives. These substitutions yield the following expression for $f(x_1, x_2)$:

$$f(x_1, x_2) = f(0, 0) + \frac{\partial y}{\partial \bar{x}_1} x_1 + \frac{\partial y}{\partial \bar{x}_2} x_2 + \frac{1}{2}\frac{\partial^2 y}{\partial \bar{x}_1^2} x_1^2$$

$$+ \frac{\partial^2 y}{\partial \bar{x}_1 \partial \bar{x}_2} x_1 x_2 + \frac{1}{2}\frac{\partial^2 y}{\partial \bar{x}_2^2} x_2^2 + \frac{1}{2}\frac{\partial^3 y}{\partial \bar{x}_1^2 \partial \bar{x}_2} x_1^2 x_2 \ .$$

Substitution of the computed numerical values for the partial derivatives yields

$$f(x_1, x_2) = f(0, 0) + 1.95 x_1 + 0.06 x_2 + \frac{1}{2}(4.32)x_1^2$$

$$- 1.30 x_1 x_2 + \frac{1}{2}(-1.02)x_1^2 x_2 \ ,$$

or, equivalently,

$$f(x_1, x_2) = f(0, 0) + 1.95 x_1 + 0.06 x_2 + 0.72(3x_1^2) - 1.30 x_1 x_2 - 0.51 x_1^2 x_2 \ .$$

Finally,

$$f(x_1, x_2) = [f(0, 0) + 1.44] + 1.95 x_1 - 0.28 x_2$$

$$+ 0.72(3x_1^2 - 2) - 1.30 x_1 x_2 - 0.17(3x_1^2 - 2)x_2 \ .$$

Equating constant terms yields

$$f(0, 0) + 1.44 = 97.98 \ ,$$

or, $f(0, 0) = 95.54$. It may be noted that $f(0, 0)$ denotes the function evaluated at the average values of x_1 and x_2. For nonlinear functions, this average may not be equal to the average value of the function. That is,

$$f(E\{x_1\}, E\{x_2\}) \neq E\{f(x_1, x_2)\},$$

and this accounts for the fact that $f(0, 0)$ does not equal 97.98 in this example.

The result of these substitutions is a Taylor series expansion that has been generated by the data. Except for the constant term, the expansion agrees identically with that obtained by the polynomial expansion. The final step would consist of attempting to deduce a functional form of f that would give rise to the computed Taylor series expansion. This approach makes it clear that every effort should be made to eliminate the noise from the response surface by statistical smoothing before attempting to deduce the functional form of f.

Determining the Dynamics of the Response Surface

The preceding developments have been concerned with the mathematical interpretation of a response surface at a given time. It is proposed, however, that the response surface can be computed at successive measurement times so that motion of the surface can be studied. It has already been noted that an empirical method for studying the motion is obtained by plotting the computed values of the coefficients at successive times. Extrapolations of these plots will yield predicted response surfaces that subsequently may be compared with observed response surfaces. By varying the time horizon of the prediction, some feedback may be obtained that will yield desired changes in measurement times and allow improved predictions over the longest possible time intervals. As described, this empirical plotting procedure does not directly yield equations of motion for the response surface. Because motion of the response surface over time is expected to result from degradations of physical components, it is expected that the surface will move in accord with time dependences associated with physical processes of certain components. Time dependences of physical processes typically are represented mathematically by differential equations. In general, then, it would be desirable to obtain a differential equation that describes the motion of the response surface.

In the physical approach to the analysis of accelerated test data, the assumption of a rate-process equation, the Arrhenius model or the Eyring model (Reference 1), for example, may give a sufficiently valid correlation, with the observed results that the general problems of fitting differential equations to data may not arise. However, if these correlations are not acceptable, some fitting method is required. One approach would consist of deducing differential equations that give rise to the observed trajectories generated by the coefficients of the response surface. Because the differential equations would not be uniquely defined by a discrete set of observed values, this approach would generate a class of differential equations. It is hoped that

some member of the class would be identifiable as an appropriate relation for some suggested physical degradation mechanism. Although the deduction of differential equations from observed trajectories generated by the coefficients is conceptually clear, it is obvious that considerable difficulty would probably be encountered in associating the equations with physical processes. The difficulty arises not from the methods of analysis but from the fact that the physical mechanisms, their interactions, and their time rates would need to be deduced from noisy data that would likely contain measurements of some irrelevant variables and would not contain measurements of some relevant variables. It is for these reasons that a mathematical response-surface approach appears to be highly attractive as a general method of approach to accelerated testing.

DATA REQUIREMENTS OF THE STATISTICAL APPROACH

It has been noted that statistical methods are typically based on averages. In general, averages are preferred over single observations because averages are more stable than the observations of which they are composed. That is, the standard deviation of an average is smaller than that of a single observation by a factor $1/\sqrt{n}$, where n denotes the number of observations in the average. In the context of an accelerated test program for batteries, the statistical approach would require a matched set of cells to be tested at each stress level in order that appropriate averages might be taken for the cells in each matched set. Because of the cost of spacecraft cells, it is desirable that a minimum number of matched cells be used at each stress level. For statistical stability, it is recommended that averages be based on observations obtained from five matched cells. The standard deviations of such averages then would be less than half that associated with single observations. Moreover, by the central-limit theorem, averages of five observations would be expected to be normally distributed, even though the individual observations of which they are composed might not be normally distributed.

A somewhat different argument may be made to determine the minimum number of stress levels to be recommended for an accelerated test. The argument begins by noting that the stress levels are to be chosen over a specific range of stress levels. The lowest stress level should correspond to the intended-use condition for the cells; the highest stress level should be the highest possible level consistent with the requirement that the dominant degradation mechanism not be changed. That is, stress levels that are too severe will yield failed cells in short time intervals, but the failures will occur for reasons that are not valid at the stress level associated with the intended-use condition.

It is often difficult to predict the maximum stress level that can be used without changing the dominant degradation mechanism. Consequently, a guess has to be made, and the data must then be analyzed to determine whether the

guess was satisfactory. In the simplest approach, the data obtained from each stress level may be examined to determine if a change in degradation mechanism is evident. This examination may sometimes be done by plotting the degradation rate as a function of a suitable measure of stress level. Linear plots may provide evidence that no change in mechanism has occurred; nonlinear plots suggest a change in mechanism. Consequently, it appears that a minimum of five stress levels are required to show the presence of two mechanisms. The two lowest stress levels would be associated with the mechanism at intended-use conditions; the two highest stress levels would be associated with a possibly different degradation mechanism at the high stress level; and the intermediate stress level would be associated with the transition between the two degradation mechanisms.

In brief, five stress levels are required to detect a change in the dominant degradation mechanism if such a change occurs. Thus, a minimum of five matched cells should be tested at each of five stress levels, varying between the intended-use condition and the maximum stress level believed to be consistent with the requirement that the dominant degradation mechanism remain unchanged.

Additional considerations indicate that it is appropriate to test more than five matched cells at each stress level in an ideal accelerated test. In particular, as shown in Section 10 on destructive testing, a total of 15 matched cells is recommended for testing at each stress level. This is done to provide for a periodic random selection and destructive examination of a cell at each stress level. This examination would be carried out a total of five times during the test program, thus increasing the recommended number of cells from five to ten for each stress level. In the ideal program, an additional increase of five cells at each stress level is recommended to provide cells for special-purpose tests, transient tests, and unforeseen experimental contingencies (i.e., accidental destruction of a cell).

SUMMARY OF STATISTICAL APPROACH

The developments of this section show that a statistical response surface provides a good basis for the analysis of accelerated test data. Such an analysis can be accomplished offline by a computer. Moreover, both an exact fit (empirical) and a smoothed fit (statistical) can be easily generated from the same data. Thus, the method provides a good tool for making the transition between an empirical and statistical analysis. The time dependence of the response surface can be obtained by plotting the coefficients of the response surface against time. This procedure will permit predictions to be made of positions of the response surface, which in turn may be interpreted as predictions of behavior of the cells on test.

Statistical arguments also show that a minimum of five matched cells should be tested at each of five stress levels. Ten additional cells at each of the five stress levels are recommended in order to provide for periodic destructive

examination of operational cells and to provide some additional cells for special-purpose tests, transient tests, and unforeseen experimental contingencies.

The following list is a summary of the data requirements for a statistical approach to an ideal accelerated test program. In addition to the 15 cells for each stress level, the list shows that voltage measurements should be taken 12 times within each charge/discharge cycle.

(1) There must be at least 15 matched cells for each stress level, with removal of two randomly selected cells at five equally spaced times during the expected duration of the test. With this procedure, five cells would be expected to complete the entire test; of the two randomly selected cells, one would be subjected to a tear-down test (discussed in Section 10) and the other would be available for special-purpose tests, transient tests, or experimental contingencies.

(2) Voltage measurements should be taken at 12 time intervals within each charge/discharge cycle. An average-voltage curve with its standard deviation would be computed for each set of matched cells. The data would be analyzed offline with statistical methods such as the response-surface technique.

5 PHYSICAL APPROACH

The empirical and statistical approaches to the accelerated testing of cells and batteries are "content independent." That is, interpretation is based upon the data obtained with no reference to the physics of the actual processes occurring inside the devices. To all intents and purposes, the empiricist and statistician see a cell or battery as a black box from which is obtained the data needed for analysis. On the other hand, the physical approach is by definition content dependent. An ideal application of the physical approach to accelerated testing and analysis of the data can be made only if the processes occurring within the cells are known or can be represented by mathematical relationships that have physical significance.

Various physical approaches to accelerated testing are summarized in a U.S. Air Force report (Reference 1). They involve the use of (1) an Arrhenius model, (2) an Eyring model, (3) stress-strain models, (4) dimensional analysis, and (5) the theory of models. Various arguments are developed regarding these approaches, but the reader should recognize that none of these approaches has widespread acceptance in battery technology. Moreover, the physical principles for choosing experiments are less developed than are the statistical and empirical techniques for working with the data after the experiments have been performed. Therefore, this section describes the positive results from an extensive mental exercise to develop an ideal physical approach to accelerated testing.

Stress-strain models are developed in detail. Each new consequence of the development is checked for consistency with known and accepted physical laws and principles. When consistency is seen, the development is carried further. Inconsistencies are avoided by using existing knowledge to guide the development.

The ideal physical accelerated test can be described in terms of the general assumptions (Reference 1) given in Section 1 and repeated here:

(1) Each cell has a quality that may be derived from physical measurements.

(2) This quality varies with time (or cycle number) and degrades after sufficient time (or number of cycles).

(3) Higher rates of degradation of quality occur at higher levels of stress.

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(4) Eventual degradation of quality to an unacceptable level will lead to failure.

(5) The relative dominance of the physical mechanisms contributing to the degradation of quality does not change during the test.

For assumptions (1) and (2), the general definition of the quality Q_s of a cell at a particular time within a charge/discharge cycle (previously given as Equation 1) is

$$Q_s = \frac{1}{\Delta s n} ,$$ (9)

where Q_s is calculated from an observed change of stress Δs at an hourly rate of charge or discharge n. Stress is said to be associated with the intensity factor of a form of energy for assumption (3). From these premises, qualities are computed as a function of changes in the operating stresses at different time intervals, or after a specified number of cycles, to obtain the time rate or cycle rate of degradation of each quality. With the quality observed in the initial cycle and a time rate of degradation of quality, extrapolation from early measurements to predict the time to failure for any predefined, low-quality value leads to the desired physical accelerated test method.

The third assumption requires that the rate of degradation of quality be accelerated with higher levels of stress. This assumption is crucial to the entire development of an ideal physical accelerated test because it demands some rigor for the meaning of "stress." Therefore, the subject of stresses will be developed, with the following results:

(1) The five general assumptions above are retained.

(2) The definition of stress for assumption (3) is changed from meaning an intensity factor to mean an intensity gradient.

(3) Equation 9 is changed to

$$Q_I = \frac{1}{\Delta I n} ,$$ (10)

where Q_I is to be calculated from observed changes of intensity factors ΔI at an hourly rate of charge or discharge n so that the original intent of quality measurements with Equation 9 is retained in Equation 10.

(4) Measurements of initial qualities and the time rate of degradation of qualities are necessary for an accelerated life test.

THE SELECTION OF STRESSES

In a report to the U.S. Air Force (Reference 1), McCallum proposed that all forms of storable energy can be described in terms of an intensity factor and an amount factor. Three requirements are given for these factors.

First, the mathematical product of the intensity factor and the amount factor must yield the dimension of work or energy.

Second, intensity factors must be consistent with the principle of higher intensity, which states—

> When two reservoirs of the same form of energy are allowed to interact with one another, energy always flows from the reservoir having the higher intensity factor.

The second law of thermodynamics is a special case of this principle as applied to heat energy. When two reservoirs of heat are allowed to interact, heat will always flow from the reservoir having the higher intensity factor (temperature).

Third, amount factors of energy must be consistent with the principle of conservation of amounts, which states for a closed system—

> When two or more reservoirs of the same form of energy are allowed to interact with one another, the sum of the amount factors remains constant.

Faraday's laws of electrolysis are special cases of the principle of conservation of amounts.

Table 14 lists 12 common forms of energy and their suggested intensity and amount factors. For each horizontal row, the intensity factor (column 3) and amount factor (column 4) satisfy the three requirements. Thus, the two factors for each row are multiplied together to give the units of work in column 5. Each intensity factor satisfies the principle of higher intensity; each amount factor satisfies the principle of conservation of amounts. It is axiomatic for this development of a physical accelerated test that any form of energy can be factored to be consistent with the listing in Table 14. Subsequently, the intensity factors are related to stress for increasing degradation rates. The intensity factors are also used for measurement of qualities with Equation 10.

To illustrate further the way in which intensity factors may be selected, consider mechanical (kinetic) energy in Table 11. From elementary mechanics, kinetic energy is given by $mv^2/2$. To factor this work function into its intensity and amount factors, one has the following choices:

(1) Amount $= m$; intensity $= v^2$.
(2) Amount $= mv$; intensity $= v$.
(3) Amount $= v$; intensity $= mv$.
(4) Amount $= v^2$; intensity $= m$.

All four choices satisfy the first criterion that amount times intensity gives work. Amount factors (1) and (2) satisfy the principle of conservation of amounts. Amount factors (3) and (4) do not satisfy the principle of conservation of amounts and, therefore, are invalid. However, choices (1) and (2) satisfy the principle of higher intensities. Therefore, choices (1) and (2) are valid for inclusion in Table 14. Actually, only choice (2) is listed, because that choice subsequently leads to a variety of consistent results in Table 15, whereas choice (1) leads to unrecognizable relationships.

Table 14—*Intensity and amount factors of various forms of energy.*

Type No.	Energy Form	Intensity Factor (Units)	Amount Factor (Units)	Work (ml^2t^{-2}) (Units)
1	Mechanical (one degree of freedom)	Force F (dyne, mlt^{-2})	Distance x (cm, l)	Fx (dyne-cm)
2	Mechanical (two degrees of freedom)	Surface tension γ (dyne-cm^{-1}, mlt^{-2})	Area a (cm^2, l^2)	γa (dyne-cm)
3	Mechanical (three degrees of freedom)	Pressure P (dyne-cm^{-2}, $ml^{-1}t^{-2}$)	Volume V (cm^3, l^3)	PV (dyne-cm)
4	Acoustical (sound)	Sound pressure p (dyne-cm^{-2}, $ml^{-1}t^{-2}$)	Volume displacement V (cm^3, l^3)	pV (dyne-cm)
5	Mechanical (rotational)	Torque T (dyne-cm, ml^2t^{-2})	Angular displacement ϕ (rad)	$T\phi$ (dyne-cm)
6	Mechanical (kinetic)	Velocity v (cm-s^{-1}, lt^{-1})	Momentum $mv/2$ (gm-cm-s^{-1} or dyne-s, ml^2t^{-1})	$mv^2/2$ (dyne-cm)
7	Gravitational (potential)	Height hG (cm^2-s^{-2}, l^2t^{-2})	Mass m (dyne-s^2-cm^{-1}, m)	mGh (dyne-cm)
8	Electrical	Voltage E [V, $(e^{-1}mlt^{-2})^{1/2}$]	Charge Q [coulomb, $(eml^3t^{-2})^{1/2}$]	EQ (V-coulomb)
9	Thermal	Temperature T (deg, θ)	Heat capacity C (cal-deg^{-1}, $ml^2t^{-2}\theta^{-1}$)	TC (cal)
10	Chemical	Osmotic pressure O (dyne-cm^{-2}, $ml^{-1}t^{-2}$)	Molar volume V_m (cm^3, l^3)	OV_m (dyne-cm)
11	Light	Frequency f (s^{-1}, t^{-1})	Illumination L (photons, or ergs, ml^2t^{-1})	fL (dyne-cm)
12	Magnetic	Magnetic potential H (dyne-cm-pole^{-1}, $m^{1/2}l^{1/2}t^{-1}\mu^{-1/2}$)	Magnetic pole α (pole, $m^{1/2}l^{3/2}t^{-1}\mu^{1/2}$)	$H\alpha$ (dyne-cm)

Some of the other energy forms in Table 14 are less or more complicated than mechanical (kinetic) energy; however, the points to be emphasized are these:

(1) All forms of energy can be factored into intensity and amount factors.
(2) Stresses for accelerated tests are to be associated with intensity gradients by means of equations yet to be derived.
(3) Changes in each intensity factor in Table 14 could be used in Equation 10 for definition of qualities, if there are practical reasons to do so.

STRESS-STRAIN RELATIONSHIPS

Generalized Stress, Strain, and Rate of Strain

In previous work on failure mechanisms and accelerated testing (Reference 1), stress-strain models are proposed as one way of describing a variety of accelerated tests. The models are based on generalized concepts of stress and strain, such as those applied to metallurgical processes (e.g., elasticity and creep). From standard reference texts (Reference 41), generalized stress and strain are defined in such a way that the product of stress and strain gives units of work per unit length, area, or volume for one-dimensional, two-dimensional, and three-dimensional geometry, respectively. For three-dimensional geometry,

$$\text{stress} \times \text{strain} = \text{work per cubic centimeter} \tag{11}$$

and

$$\text{stress} \times \text{rate of strain} = \text{work per cubic centimeter per second}$$

$$= \text{power per cubic centimeter,} \tag{12}$$

when volumes are measured in cubic centimeters.

With Equations 11 and 12, Reference 1 suggested how the definitions of quality in Equation 9 might describe a stress/rate-of-strain relationship for an electrochemical cell. It then suggested that the amount factors in energy types 1, 3, 8, and 9 of Table 14 could be related quantitatively to the hourly rate of discharge in Equation 9. Thus, the four stresses related to force, pressure, voltage, and temperature could be described by a stress-strain relationship analogous to Hooke's law:

$$\text{Stress is proportional to strain.} \tag{13}$$

The four could also be described by a stress/rate-of-strain relationship analogous to Newton's law of viscous flow:

$$\text{Stress is proportional to rate of strain.} \tag{14}$$

Reference 1 also suggested that stresses can be created internally or externally relative to the spacecraft cell. These four stresses, controlled four ways,

theoretically give 16 methods for constructing accelerated tests. Hypothetically, up to 16 factorial combinations might exist if the 16 methods were independent of one another.

As part of the goal of devising an ideal accelerated test, these concepts will be extended, modified, and tested in connection with the energy forms in Table 14. Equations 11 through 14 will be maintained. In Table 14, sound energy (4), rotational energy (5), potential energy (7), and magnetic energy (12) will be dropped from further consideration because they are of little practical significance in the testing of cells. The intensity and amount factors will be retained, with the exception of chemical energy (1) and thermal energy (9). The intensity factor for chemical energy will be changed from pressure to concentration because the two units are related through Van't Hoff's relationship (Reference 42). The amount factor for chemical energy will be changed from molar volume to number of moles, and the amount factor for thermal energy will be changed from heat content (calories per degree) to heat (calories), for reasons that will be explained.

Generalized Fluxes

In Table 14, consideration was given to Fick's laws of diffusion and the possible connection between the variables in Fick's laws and the amount and intensity factors. Fick's first law of diffusion is

$$\text{flux} = D\frac{dC}{dx} , \tag{15}$$

where D is a diffusion constant, C is concentration (moles per cubic centimeter), and x is the distance perpendicular to the flux; flux is measured in moles per square centimeter per second. Fick's second law is

$$\frac{dC}{dt} = D\frac{d(\text{flux})}{dx}$$

$$= D\frac{d^2C}{dx^2} , \tag{16}$$

where t is time. From Equations 15 and 16, it was recognized that concentration C is proportional to osmotic pressure O; therefore, either concentration or osmotic pressure could be placed in the intensity-factor column of Table 14 for energy type 6. Moreover, through the molecular volume data from conventional handbooks, moles (or molecules) are directly convertible to volume and may, therefore, be placed in the amount-factor column of Table 14 for energy type 6. A consequence of these substitutions is that their product yields osmotic chemical work, as in the work column of Table 14.

A much more significant consequence of this interchange of units is that Fick's laws may be generalized for all forms of energy in terms of intensity and amount factors. Thus,

$$\text{flux} = \text{amount per square centimeter per second}$$

$$= \frac{1}{a}\frac{\partial A}{\partial t}$$

$$= k_{17}\frac{\partial I}{\partial x} \, , \tag{17}$$

where a is area in square centimeters. Equation 17 will be called the "flux generality"; it is read as follows: The change in amount per unit area per unit time is proportional to the intensity gradient.

This flux generality is obviously limited to three-dimensional space because the intensity gradient must be perpendicular to the area. Even so, application of the flux generality to the other energy forms in Table 11 offers an excellent opportunity to see whether the intensity and amount factors are chosen properly.

More important to the subject of accelerated tests is the fact that Equation 17 leads to a generalized stress/rate-of-strain relationship given by Equation 12 when strain is equated to amount per unit area and stress is equated to the intensity gradient. Then, fluxes are equivalent to a rate of strain; therefore,

$$\text{stress} \times \text{rate of strain} \equiv \text{intensity gradient} \times \text{flux}$$

$$= \left(\frac{\partial I}{\partial x}\right)\left(\frac{1}{a}\frac{\partial A}{\partial t}\right)$$

$$\equiv \text{power per unit volume.} \tag{18}$$

Moreover,

$$\text{stress} \times \text{strain} = \text{intensity gradient} \times \text{amount/area}$$

$$= \text{work per unit volume.} \tag{19}$$

It follows from Equations 18 and 19 that different stress levels in an accelerated test are associated with values of an intensity gradient and with strains and rates of strain. These relationships will be developed for the various kinds of energy applicable to spacecraft batteries; the intent is to build a logical and valid basis for ideal physical accelerated life tests.

In Table 15, columns 2, 4, and 5 have been repeated from Table 14, with the changes in energy types 5 and 6 previously mentioned. Column 3 has been added to emphasize that neither the amount nor the intensity factors are, by themselves, energy forms. For example, for type 3, mechanical energy is obtained from the product of pressure and volume, but the amount column is

Table 15—Generalized stress/strain and stress/rate-of-strain relationships.

Type No.	Energy Form	Energy Source	Intensity Factor I	Amount Factor A	Flux Generality $\frac{1}{a}\frac{\partial A}{\partial t} = k_{17}\frac{\partial I}{\partial x}$	Conservation Generality $\frac{\partial I}{\partial t} = k_{26}\frac{\partial^2 I}{\partial x^2}$	Stress-Strain Generality $\frac{\partial I}{\partial x} = k_{36}\frac{A}{a}$	Impulse-Amount Generality $\Delta I = k_{42}\frac{\partial A}{\partial t}$	Impulse-Rate Generality $\Delta I = k_{53}\frac{\partial^2 A}{\partial t^2}$
1	Mechanical (one degree of freedom)	Motion	Force F	Distance x	Not appropriate	Not appropriate	Not appropriate	$\Delta F = k_{43}\frac{\partial x}{\partial t}$ (Newton's first law, Stokes' law)	$\Delta F = k_{55}\frac{\partial^2 x}{\partial t^2}$ (Newton's second law)
2	Mechanical (two degrees of freedom)	Liquids	Surface tension γ	Area a	Not appropriate	Not appropriate	Not appropriate	$\Delta\gamma = k_{45}\frac{\partial a}{\partial t}$	$\Delta\gamma = k_{53}\frac{\partial^2 a}{\partial t^2}$
3	Mechanical (three degrees of freedom)	Liquids or gases	Pressure P	Volume V	$\frac{1}{a}\frac{\partial V}{\partial t} = k_{20}\frac{\partial P}{\partial x}$ (Poiseuille's law)	$\frac{\partial P}{\partial t} = k_{27}\frac{\partial^2 P}{\partial x^2}$	$\frac{\partial P}{\partial x} = k_{38}\frac{V}{a}$ (sound energy)	$\Delta P = k_{46}\frac{\partial V}{\partial t}$ (Poiseuille's law)	$\Delta P = k_{53}\frac{\partial^2 V}{\partial t^2}$
4	Electrical	Electricity	Voltage E	Charge Q	$\frac{1}{a}\frac{\partial Q}{\partial t} = k_{23}\frac{\partial E}{\partial x}$ (Ohm's law)	$\frac{\partial E}{\partial t} = k_{28}\frac{\partial^2 E}{\partial x^2}$ (Ohm's law)	$\frac{\partial E}{\partial x} = k_{37}\frac{Q}{a}$ (capacitance relationship)	$\Delta E = k_{47}\frac{\partial Q}{\partial t}$ (Ohm's law)	$\Delta E = k_{56}\frac{\partial^2 Q}{\partial t^2}$ (inductance relationship)
5	Thermal	Heat	Temperature T	Heat q (calories)	$\frac{1}{a}\frac{\partial q}{\partial t} = k_{24}\frac{\partial T}{\partial x}$ (Fourier's law)	$\frac{\partial T}{\partial t} = k_{29}\frac{\partial^2 T}{\partial x^2}$ (Fourier's law)	$\frac{\partial T}{\partial x} = k_{36}\frac{q}{a}$	$\Delta T = k_{48}\frac{\partial q}{\partial t}$ (Fourier's law)	$\Delta T = k_{53}\frac{\partial^2 q}{\partial t^2}$
6	Chemical	Chemical species in solution	Concentration C	Moles M	$\frac{1}{a}\frac{\partial M}{\partial t} = k_{25}\frac{\partial C}{\partial x}$ (Fick's first law)	$\frac{\partial C}{\partial t} = k_{30}\frac{\partial^2 C}{\partial x^2}$ (Fick's second law)	$\frac{\partial C}{\partial x} = k_{39}\frac{M}{a}$	$\Delta C = k_{49}\frac{\partial M}{\partial t}$ (mass action law)	$\Delta C = k_{53}\frac{\partial^2 M}{\partial t^2}$
7	Kinetic	Motion	Velocity v	Momentum mv	$\frac{1}{a}\frac{\partial mv}{\partial t} = k_{31}\frac{\partial v}{\partial x}$ (Bernoulli's theorem)	$\frac{\partial v}{\partial t} = k_{33}\frac{\partial^2 v}{\partial x^2}$	$\frac{\partial v}{\partial x} = k_{36}\frac{mv}{a}$	$\Delta v = k_{50}\frac{\partial mv}{\partial t}$ (Newton's first law, Stokes' law)	$\Delta v = k_{53}\frac{\partial^2 mv}{\partial t^2}$ (Hooke's law)
8	Light	Radiation	Frequency f	Illumination L (number of photons)	$\frac{1}{a}\frac{\partial L}{\partial t} = k_{34}\frac{\partial f}{\partial x}$ (the rad)	$\frac{\partial L}{\partial t} = k_{17}\frac{\partial^2 L}{\partial x^2}$	$\frac{\partial f}{\partial x} = k_{36}\frac{L}{a}$	$\Delta f = k_{51}\frac{\partial L}{\partial t}$ (Planck's law)	Not appropriate

not one of mechanical energy but of liquid, gas, or some other tangible material associated with the performance of mechanical work.

Substitution of the intensity and amount factors from columns 4 and 5 into the flux generality of Equation 17 leads to the following relationships for mechanical energy (type 3):

Mechanical (3): The flux of volume per unit area per unit time is proportional to the pressure gradient:

$$\frac{\partial V}{a \partial t} = k_{20} \frac{\partial P}{\partial x} . \tag{20}$$

Equation 20 is a statement of Poiseuille's law for liquid flow through capillary tubes of radius r:

$$\frac{\partial V}{\pi r^2 \partial t} = \frac{r^2}{8\eta} \frac{\partial P}{\partial x} , \tag{21}$$

where η is the viscosity of the liquid and $r^2/8\eta$ is equivalent to k_{20} in Equation 20.

Since the change of volume on the left-hand side of Equation 20 is equal to cross-sectional area times change of distance, the areas cancel out and the equation may be written as

$$\frac{\partial x}{\partial t} = k_{22} \frac{\partial P}{\partial x} . \tag{22}$$

Equation 22 is read, "Velocity is proportional to the pressure gradient." This statement is an empirical law used by meteorologists (Reference 43) noting that wind velocities are proportional to pressure gradients. Here, however, an empirical or experimental law has been derived from abstract principles of amounts and intensities having no limitations to the subject matter being considered. This agreement of predictions from starting principles about amounts and intensities with observations from published knowledge is taken as evidence that the starting principles are correct. For an ideal physical test, then, one possible stress is a pressure gradient associated with a flux, as, for example, in gas movements between plates.

In like manner, the validity of the flux generality can be tested by substitution of the other factors from columns 4 and 5 of Table 15 into Equation 17, as follows:

Electrical (4): The number of coulombs per unit area per unit time is proportional to the voltage gradient:

$$\frac{\partial Q}{a \partial t} = k_{23} \frac{\partial E}{\partial x} . \tag{23}$$

The left-hand side of Equation 23 has the dimensions of current density, and the proportionality constant has a dimension of conductivity with units of

mhos per centimeter. Equation 23 is, therefore, a form of Ohm's law. It was derived from principles having nothing to do with electricity; such a derivation is strong support for Equation 17 because Ohm's law is based on experimental observations and has not been derived heretofore from independent concepts. From the viewpoint of a physical accelerated test, the electrical stress associated with Equation 23 is the voltage gradient.

Thermal (5): The calories per unit area per unit time are proportional to the temperature gradient:

$$\frac{\partial q}{a \partial t} = k_{24} \frac{\partial T}{\partial x} .$$

(24)

Substitution of the intensity and amount factors from Table 15 leads to Biot-Fourier's law of heat conduction. The amount factor for heat has been listed as calories in Table 15, whereas calories per degree was listed in Table 14. This change of units was done, first, so that energy type 5 in Table 15 might be made consistent with other information in the table. The amount factor thereby is made consistent with the principle of conservation of amounts, but the product of intensity (column 4) and the amount factor (column 5) no longer leads to the proper dimension for thermal work.

With the recognition of a fundamental problem in the science of heat, it seems advisable to pass on to the relevancy of heat and temperature to accelerated tests. Temperature is often suggested as a stress factor for accelerated life tests, and its positions in Tables 14 and 15 are consistent with that general presumption. The main significance of Equation 24 is that it leads to the inference that a heat flux will have associated with it a temperature gradient and, therefore, a corresponding stress level for accelerating the degradation of battery qualities. Also, the derivation of the time-honored heat equation (Equation 24) from the consideration of nonthermal relationships provides additional confirmation for the validity of Equation 17.

Chemical (6): The moles per unit area per unit time are proportional to the concentration gradient:

$$\frac{\partial M}{a \partial t} = k_{25} \frac{\partial C}{\partial x} .$$

(25)

This substitution of the intensity and amount factors from Table 15 into Equation 17 was the origin of Equation 17, as previously described. Equation 17 is repeated above as Equation 25 in this development. The proportionality constant k_{25} is the well-known diffusion constant D. One important consequence of Equations 17 or 25 and 18 is that a concentration gradient in a battery is predicted to be a stress.

Another important consequence of Equation 25 is the "conservation generality" in column 7 of Table 15:

$$\frac{\partial I}{\partial t} = k_{26} \frac{\partial^2 I}{\partial x^2} .$$

(26)

Equation 26, which is read, "The time rate of change of intensity is proportional to the second derivative of intensity with respect to distance," may be recognized as Fick's second law of diffusion, previously given as Equation 16. The second derivative in Equation 26 will be recognized as the change of flux with respect to distance.

Just as the proportionality constant D in Equation 15 is identical with the constant D in Equation 16, it follows that k_{25} is identical with k_{26} for chemical-energy factors. The importance of Equation 26 in connection with accelerated tests is that it provides physical and mathematical relationships for the determination of the proportionality constants in stress/rate-of-strain equations through the observation of transient phenomena.

Thus, for the ideal test involving a pressure gradient as a stress level, a series of measurements of a time rate of pressure change could provide an additional tool for measuring the rate at which the stress/rate-of-strain coefficient is changing:

$$\frac{\partial P}{\partial t} = k_{27} \frac{\partial^2 P}{\partial x^2}$$

$$= k_{20} \frac{\partial^2 P}{\partial x^2} , \tag{27}$$

where $k_{27} = k_{20}$ and the volume flux is nonuniform in direction x. Similarly, for the electrical, thermal, and chemical energies in column 7 of Table 15, a measure of the change of intensity with time could be used as a measure of changing fluxes and stress levels, as follows:

Electrical:
$$\frac{\partial E}{\partial t} = k_{28} \frac{\partial^2 E}{\partial x^2}$$

$$= k_{23} \frac{\partial^2 E}{\partial x^2} , \tag{28}$$

Thermal:
$$\frac{\partial T}{\partial t} = k_{29} \frac{\partial^2 T}{\partial x^2}$$

$$= k_{24} \frac{\partial^2 T}{\partial x^2} . \tag{29}$$

Chemical:
$$\frac{\partial C}{\partial t} = k_{30} \frac{\partial^2 C}{\partial t^2}$$

$$= D \frac{\partial^2 C}{\partial x^2} . \tag{30}$$

Returning to the flux generality in column 6 of Table 15:

Kinetic (7): The change of momentum per unit area per unit time is proportional to the velocity gradient:

$$\frac{\partial mv}{a\partial t} = k_{31}\frac{\partial v}{\partial x}.$$ (31)

Since, by Newton's second law of motion, the change of momentum with respect to time is equivalent to force, the left-hand side of Equation 31 has units of dynes per square centimeter, which is pressure. Therefore,

$$P = k_{32}\frac{\partial v}{\partial x}.$$ (32)

Equation 32 is an inversion of Equation 21, which is an accepted relationship in the science of meteorology (Reference 43). Equation 32, a special case of Bernoulli's theorem of liquid flow at constant potential energy, also relates pressure with a momentum flux. It suggests that the gas pressure in a closed container is proportional to the velocity gradient of the centers of mass of the molecules striking the container walls. This suggestion is believed to be a new concept in the kinetic theory of gases that could account for the different behavior of gases having different elastic constants. Equation 32 also suggests that the pressure on a satellite during its reentry is proportional to its velocity gradient; similarly, Equation 32 suggests that the pressure exerted on a battery case is proportional to the velocity gradient of the battery during a vibration test. Therefore, a stress factor for a vibration test is, by inference, the velocity gradient. (The velocity is the product of amplitude and frequency of vibration; the distance over which the velocity changes direction must be known to calculate the velocity gradient.) Moreover, by analogy with the other energy forms in Table 15, the conservation generality of column 7 is expected to apply so that

$$\frac{\partial v}{\partial t} = k_{33}\frac{\partial^2 v}{\partial x^2}.$$ (33)

(All of the above suggestions appear to be amenable to experimental validation. If future work were to validate the suggestions, the results would provide strong support for Equation 17 and the concepts being developed in this section.)

Light (8): The number of photons per unit area per unit time is proportional to the frequency gradient:

$$\frac{\partial L}{a\partial t} = k_{34}\frac{\partial f}{\partial x}.$$ (34)

If each photon in Equation 34 is multiplied by Planck's constant, the left-hand side of the equation then assumes the dimension of an action flux:

$$\frac{\text{erg-second}}{\text{square-centimeter-second}} = k_{35}\frac{\partial f}{\partial x} = \frac{\text{ergs}}{\text{square centimeter}}.$$ (35)

Equation 35 is apparently a new relationship. It suggests that an appropriate definition of light intensity should show a proportionality to a frequency gradient. The equation also suggests that radiation damage should be directly proportional to a frequency gradient during absorption. The concept of a frequency gradient, which has been evoked elsewhere (Reference 44), brings to mind a possibly new explanation for the "red shift" phenomenon in astronomy.

Ideally, at least, light energy or some other form of radiation would be one of the sources for accelerating degradation of quality. A frequency gradient would be the stress factor; a photon flux would be the rate of strain. The product of the stress and the rate of strain, then, is closely related to the radiological unit for absorption rates recently described by Henley and Johnson (Reference 45):

> Many units have been devised to characterize the absorption of ionizing radiation. In recent years, however, there has been a general acceptance of the recommendations of the ICRU [International Commission on Radiation Units] that the use of certain units be restricted as follows: 1 rad = 100 erg/g = 6.24 × 10^{13} eV/g—the absorbed dose rate is the quotient of the rad divided by a unit of time, e.g., rad/s.

These definitions are quoted to suggest that if the rad were defined officially in terms of ergs per cubic centimeter rather than ergs per gram (the two definitions differ only by the density of the absorbing material), absorption phenomena would be consistent with the flux generality and all the energy forms in Table 15.

Summary of Stress/Rate-of-Strain Relationships

Stress factors that have been suggested for the ideal physical accelerated test are summarized in Table 16; they are derived from the flux generality of Equation 17, repeated here for convenience:

$$\text{amount per square centimeter per second} = \frac{1}{a} \frac{\partial \,(\text{amount})}{\partial t}$$

$$= k_{17} \frac{\partial \,(\text{intensity})}{\partial x} \ .$$

In the ideal accelerated test, the various physical stresses in Table 13 will be separated, combined, and controlled in order that the dominant failure mechanisms will be accelerated and retained during a shortened test time.

Generalized Strains

Equations 12, 14, and 17 through 35 have shown a large number of rate-of-strain relationships. All of them could be used in the ideal physical accelerated test to accelerate the rate of degradation of quality. The derivation of accepted physical laws and well-known relationships in columns 6 and 7 of

Table 15 gives strong credence to the physical approach being proposed. However, simultaneous attempts to derive a similar generalized stress-strain relationship (Equation 13) have been less certain. It is true that Table 16 lists six kinds of strain with seven different units; but all the strains satisfy a stress/rate-of-strain proportionality called for in Equation 14. Some of them, however, also satisfy the stress-strain proportionality called for in Equation 13 for three-dimensional geometry:

$$\frac{\partial I}{\partial x} = k_{36} \frac{A}{a} \ . \tag{36}$$

The three-dimensional stress-strain relationship at the top of Table 16 substituted into Equation 36 leads to the relationship that the pressure gradient between stored liquids is proportional to the volumes of liquid stored per unit area between the reservoirs:

$$\frac{\partial P}{\partial x} = k_{37} \frac{V}{a} \ . \tag{37}$$

Of course, Equation 37 applies only to cubical containers in which the three spatial dimensions are orthogonal, as described previously for Equation 19.

The electrical stress and strain leads to

$$\frac{\partial E}{\partial x} = k_{38} \frac{Q}{a} \ . \tag{38}$$

which is the standard capacitance equation (Reference 46) for parallel-plate condensers.

With further development of Equation 36, a chemical stress could also be expected:

$$\frac{\partial C}{\partial x} = k_{39} \frac{M}{a} \ . \tag{39}$$

An example of Equation 39 is osmosis after equilibrium, where M/a is the moles per unit area of membrane and $\partial C/\partial x$ is the concentration gradient across the membrane of thickness ∂x.

Table 16—*Summary of stresses and strains for rechargeable cells from rate-of-strain relationships.*

Stress	Associated Strain	Rate-of-Strain Equation No.
Pressure gradient	Volume flowing per unit area	19
Voltage gradient	Coulombs per unit area	23
Temperature gradient	Calories flowing per unit area	24
Concentration gradient	Moles flowing per unit area	25
Velocity gradient	Change of momentum per unit area	31
Frequency gradient	Photons absorbed or emitted per unit area	34

Thermal energy (5), kinetic energy (7), and light energy (8) are not usually thought of as being stored in a static condition. If they were so stored, thermal, kinetic, and light forms of energy would have the following stress-strain relationships:

(1) Thermal energy: The temperature gradient is proportional to calories per unit area.

(2) Kinetic energy: The velocity gradient is proportional to impulse per unit area.

(3) Light energy: The frequency gradient is proportional to the action per unit area.

Each of these stress-strain relationships would be recognized and utilized in the development of an ideal accelerated test.

It follows that the ratio of coefficients k_{36} and k_{17} has the dimension of time. This ratio of coefficients is analogous to RC time constants in electrical circuitry and to the elastic/viscous-flow coefficients of spring and dash-pot circuits (Reference 1). Similar time constants will exist for any physical system having simultaneous flux (as described by Equation 17) and storage (as described by Equation 36) of the same form of energy; that is,

$$\frac{k_{36}}{k_{17}} = \tau_{40} \tag{40}$$

Equation 40 also suggests the use of transient measurements as a means of determining the coefficients associated with stress-strain and stress/rate-of-strain equations.

The stress-strain relationship of Equation 36 indicates one of the reasons why the definition of battery quality in Equation 10 must specify a time of charge and discharge within each cycle. Thus, the definition

$$Q_I = \frac{1}{\Delta In}$$

leads to a quality measurement that depends on the time of charge or discharge t'. Also, the amount and intensity factors in Equation 36 depend on t'. Therefore, quality could also be defined in terms of charge and discharge times:

$$Q_I' = Q_I t'$$

$$= \frac{t'}{\Delta In} . \tag{41}$$

Since stresses in Table 16 have been identified as intensity gradients and the strains as amounts per unit area, the degradation of voltage quality given by Equation 41 would be accelerated by the stress given by Equation 38. The specific use of Equations 37 and 39 to accelerate the quality described by Equation 41 requires a quantitative relationship between coulombs charged or

discharged with volume (Equation 37) and with moles (Equation 39). Both quantitative relationships exist in Faraday's laws of electrolysis.

It should be noted that the qualities of Equations 10 and 41 are not the same as the stresses in Table 16, because qualities have been defined in terms of intensity factors in column 4 of Table 15, whereas stresses have been defined in terms of intensity gradients in columns 6 and 8. Thus, qualities will be measured in terms of pressures, voltages, temperatures, and so forth, whereas stresses will be used (whether measured or not) as pressure gradients, voltage gradients, temperature gradients, and so forth. This situation is exactly analogous to the difference between resistances and resistivities or between flows (amount per unit time) and fluxes (amount per unit area per unit time). The differences between intensity factors and intensity gradients should become even more apparent with the following developments.

The Impulse-Amount Generality

In Table 15, the impulse-amount generality in column 9, based on the intensity and amount factors in columns 4 and 5, states simply that the change of intensity ΔI is proportional to the time rate of change of the amount $\partial A / \partial t$:

$$\Delta I = k_{42} \frac{\partial A}{\partial t} . \tag{42}$$

Equation 42 is called the impulse-amount generality because the coefficient k_{42} has the dimension of impulse per unit of amount. It differs from the flux generality of Equation 17 in that geometric, orthogonal dimensions are not used.

Substituting the intensity and amount factors of Table 15 into Equation 42 yields the following:

Mechanical (1): Force is proportional to velocity:

$$\Delta F = k_{43} \frac{\partial x}{\partial t} . \tag{43}$$

Equation 43 is a relationship used to derive Stokes' law of viscous flow for falling bodies:

$$F = 6\pi\eta r v , \tag{44}$$

where η is the viscosity of the fluid through which a sphere of radius r is falling at a velocity $v = dx/dt$. Then, $k_{43} = 6\pi\eta r$. The proportionality constant k_{43} is frequently called the moving-friction coefficient. Equation 43 is an empirical law based on many experimental observations. Its derivation from abstract principles is not normally found in the literature; however, a statistical derivation is possible (Reference 47).

Surface (2): A change of surface tension is proportional to the time rate of change of area:

$$\Delta\gamma = k_{45} \frac{\partial a}{\partial t} . \tag{45}$$

This quantitative dependence of surface tension on changing areas has not been found in the literature; however, all textbooks on physical chemistry report that surface-tension measurements should be made under conditions approaching steady state in order to obtain reproducible and reliable data.

Mechanical (3): A change of pressure is proportional to the volume flow rate:

$$\Delta P = k_{46} \frac{\partial v}{\partial t} . \tag{46}$$

Equation 46 is a special case of Poiseuille's law for fluid flow (previously given as Equation 21) when path length and cross-sectional area are constant. For example, the volume rate of water flowing from a water faucet is proportional to the pressure drop within the faucet.

Electrical (4): A change of voltage is proportional to the coulombs per second:

$$\Delta E = k_{47} \frac{\partial Q}{\partial t} . \tag{47}$$

Equation 47 is a statement of Ohm's law of electrical conductance in which k_{47} is the circuit resistance. As has been stated, Ohm's law is an empirical law based on experimental observations—it has not been derived from abstract principles having nothing to do with electricity; its derivation from Equation 42 lends credibility to the principles involved.

Thermal (5): A temperature drop is proportional to the rate of flow of calories:

$$\Delta T = k_{48} \frac{\partial Q}{\partial t} . \tag{48}$$

Equation 48 is Fourier's law for heat conduction.

Chemical (6): A change in concentration is proportional to the moles per second increasing or decreasing:

$$\Delta C = k_{49} \frac{\partial M}{\partial t} . \tag{49}$$

Equation 49 leads to a form of the mass-action law of equilibrium when applied to both reactants and products.

Kinetic (7): A change of velocity is proportional to the time rate of change of momentum:

$$\Delta V = k_{50} \frac{\partial mv}{\partial t} . \tag{50}$$

Equation 50 is the same as Equation 43, because $\partial mv/\partial t = \Delta F$. Therefore, the same relationship for two forms of mechanical energy (1 and 7) was derived from the same generality of Equation 42. This agreement supports the validity of Equation 42 as well as the factors chosen for columns 4 and 5 in Table 15.

Light (8): A change in frequency is proportional to the rate of loss of photons:

$$\Delta f = k_{51} \frac{\partial L}{\partial t} . \tag{51}$$

When the number of photons L is multiplied by Planck's constant, Equation 51 becomes

$$\Delta f = k_{52} \Delta \text{ ergs,} \tag{52}$$

which is Planck's law for light energy, in which k_{52} is the reciprocal of Planck's constant. This derivation of Planck's law from the impulse--amount generality is the principal reason why the intensity and amount factors for light have been retained in Table 15 as further evidence for a valid classification of dimensions.

The Impulse-Rate Generality

The impulse-rate generality is also based on the intensity and amount factors in columns 4 and 5 of Table 15 and states simply that the change of intensity ΔI is proportional to the second derivative of amount with respect to time:

$$\Delta I = k_{53} \frac{\partial^2 A}{\partial t^2} \tag{53}$$

Equation 53 is called the impulse-rate generality because the coefficient k_{53} has the dimension of impulse divided by the time rate of change of amount. Therefore, the ratio of k_{53} to k_{42} has the dimension of time:

$$\frac{k_{53}}{k_{42}} = \tau_{54} . \tag{54}$$

This ratio will provide a characteristic time constant τ_{54} that is analogous to the time constant for an inductive-resistive electrical circuit.

Substituting the intensity and amount factors of columns 4 and 5 from Table 15 into Equation 53 leads to the following relationships:

Mechanical (1): The change of force is proportional to the second derivative of distance with respect to time:

$$\Delta F = k_{55} \frac{\partial^2 x}{\partial t^2} , \tag{55}$$

wherein the constant k_{55} is mass. This is Newton's second law of motion: Force is proportional to acceleration. Such a derivation of Newton's second law from abstract principle is strong confirmation of the validity of the abstract principles upon which the derivation is based.

Electrical (4): The change of voltage is proportional to the second derivative of coulombs with respect to time:

$$\Delta E = k_{56} \frac{\partial^2 Q}{\partial t^2} , \tag{56}$$

in which k_{56} is the self-inductance coefficient. Equation 54 is the accepted law of electromagnetic induction.

Similar relationships have been deduced from the impulse-rate generality of Equation 53 and are tabulated in column 10 of Table 15. From these considerations, a total relationship between certain intensities and their corresponding amount factors in columns 4 and 5 was noted:

$$I = k_{57}A + k'_{57}\frac{\partial A}{\partial t} + k''_{57}\frac{\partial^2 A}{\partial t^2} \, . \tag{57}$$

Examples of Equation 57 are the equation of motion of a damped, simple harmonic oscillator (Reference 48) or the equation for the total voltage drop in a simple electrical circuit containing a capacitance, a resistance, and a self-inductance (Reference 46). In the latter example, the coefficients k_{57}, k'_{57}, and k''_{57} can be identified in physical terms as the reciprocal capacitance, the resistance, and the self-inductance, respectively. Also, by analogy, $k'_{57} = k_{42}$ and $k''_{57} = k_{53}$.

In Equation 57, the first term (with coefficient k_{57}) will have values other than zero for steady-state conditions of stored energy, as in an electrical capacitor, as well as for dynamic forms of the energy. Conversely, the second and third terms of Equation 57 will have nonzero values only for dynamic conditions, as when electrical current flows. The first and second terms in Equation 57 will have nonzero values whether the amount rate is steady state or changing, whereas the third term (with coefficient k''_{57}) will have values other than zero only when the amount rate is changing. These distinctions between the various terms of Equation 57 could be used to distinguish between the various kinds of stresses contributing to the total stress on a battery because of the different ways intensity factors can be changed.

Interaction of Stresses

With eight forms of energy having the numerous relationships indicated in Table 12, the need to consider how to use, or to avoid using, the various combinations in the ideal accelerated test is apparent. Thus, Table 16 was followed by this conclusion:

> In the ideal accelerated test, the various physical stresses in Table 16 will be separated, combined, and controlled in order that the dominant failure mechanisms will be accelerated and retained during a shortened test time.

The following paragraphs are aimed at answering how to separate, combine, and control the various physical stresses.

The major tools for handling the various interactions of energy are the conservation laws. The first law of thermodynamics is the most inclusive (Reference 49):

> Energy can neither be created nor destroyed; when one form of energy disappears, another form of energy always appears in equivalent quantity.

This law is important for applying the equations in Table 15 to cells or batteries because it requires quantitative accounting for all the energy. For

example, as chemical energy (6) is converted into electrical energy (4), there will be changes in thermal energy (5), mechanical energy (1), surface energy (2), volume expansion energy (3), and kinetic energy (7). With all events, the total energy within a closed system does not disappear. That is, for a closed system, in the thermodynamic sense of including the cell or battery and its environment, the total energy will be conserved:

$$\text{Total energy} = \text{sum of energies for all processes.} \qquad (58)$$

Therefore, if the proportions of various energies as a function of strain and of rate of strain are known, the various physical stresses can be deduced from their corresponding relationships in Table 15. For example, if 20 W-hr of electrical energy are taken from a sealed cell, there will be X_1 watt-hours of heat generated plus X_2 watt-hours of mechanical work plus X_3 watt-hours of chemical work at some given rate η_1. At a different rate η_2, and for the same electrical output of 20 W-hr, the proportions of X_1, X_2, and X_3 may be different, but the total energy must remain constant so that energy is neither created nor destroyed. Equation 58 must be satisfied.

Another conservation tool for separating, combining, and controlling physical stresses may be deduced from the principle of conservation of amounts. In stating this principle prior to Table 14, emphasis was given to the interaction between two reservoirs of the same energy form:

When two or more reservoirs of the same form of energy are allowed to interact with one another, the sum of the amount factors remains constant.

Faraday's laws of electrolysis are cited as well-known examples of the principle of conservation of amounts. However, in the development of an ideal physical accelerated test, it should be recognized that the principle of conservation of amounts can be applied to conversions of energy forms. For energy conversions, this principle is applied to conserve amounts, while at the same time, the concept of efficiency may be introduced. Thus, for example, with Faraday's laws of electrolysis, every coulomb (the amount factor) shows up as electrons, ions, molecules, or free radicals and not one net electron is created or destroyed. However, in a nickel-cadmium cell, a loss of electron at the positive electrode may oxidize nickel hydroxide during charging or may cause the evolution of oxygen gas. The efficiency of either oxidation process could lie between 0 and 100 percent, inclusive; but the total balance of electrons, without exception, is always 100 percent. Similarly, every photon either exists or is annihilated by reaction, according to Einstein's law of photoelectricity. Every molecule in solution either passes through a membrane by osmotic pressure or does not pass through. There is no uncertainty about such events, and amount factors in a closed system remain constant:

The sum of amount factors entering =

$$\text{the sum of amount factors stored and leaving.} \qquad (59)$$

A consequence of Equation 59 and the principle of conservation of amounts is that the fluxes of Equation 17 must also be conserved:

The sum of fluxes entering = the sum of fluxes leaving and interacting. (60)

For example, the flux of photons entering is equal numerically to the flux of photons transmitted plus the flux of amount factors created by the absorption of photons.

This conservation of amounts and fluxes means all energy forms in Table 15 can be separated, combined, or controlled in a quantitative fashion, and Equations 59 and 60 must be satisfied as well as Equation 58. Once amounts and appropriate geometries have been determined, the generalities of columns 6 through 10 in Table 15 give a relationship to intensities and stresses and, through Equations 10 or 41, to cell or battery qualities. The ideal accelerated test, then, will measure initial qualities and time rate or cycle rate of quality degradation at high stress levels. Then, extrapolations to normal or operational stress levels will allow predictions of times to cell failures under normal operating conditions. Moreover, because the qualities and stresses will have been based on quantitative work, stress-strain, and stress/rate-of-strain relationships, the failure mechanisms will have a physical meaning.

BATTERY FAILURES AND FAILURE MECHANISMS

Failure Definition

Failures for sealed spacecraft cells or batteries have been defined in previous work for the U.S. Air Force (Reference 1). In essence, a cell or battery has failed when it is unable to deliver on discharge or accept on charge a predetermined current for a specified length of time within a certain voltage tolerance set by the user.

To develop failure analysis procedures, it was necessary to define failure modes, failure determinants, and failure mechanisms. These definitions are repeated below because the ideal physical accelerated test will shorten the time to failure without changing the failure mode, the failure determinant, or the failure mechanism. Thus, these modes, determinants, and, especially, their mechanisms should be properly identified:

    (1) Failure dimension: volts, amperes, or time out of tolerance
    (2) Failure mode: failure dimension that went out of tolerance
    (3) Failure determinant: cause of failure mode
    (4) Failure mechanism: cause of failure determinant

For example, the voltage (dimension) may fall below an acceptable level on charge (mode) because of an electrical short between the electrodes (determinant) caused by the migration and reprecipitation of negative electrode material in the separator (mechanism). Overall, a degradation in voltage quality is observed.

With reference to Equation 10, this definition of failure could be related through voltage or hourly rate to battery electrical quality. That is, a battery will have failed when its electrical quality, from Equation 10, has become unacceptable to the user. The other definitions of quality to be associated with the stresses in column 6 of Table 15 or column 1 of Table 16 will not be used here as a definition of failure because the users of spacecraft batteries can be expected to accept any pressure, temperature, or concentration, provided electrical quality remains acceptable. From a physical point of view, therefore, the nonelectrical energy forms in Tables 14 and 15 are of interest for failure analysis and for accelerated testing only insofar as the nonelectrical processes can be related to electrical qualities.

Failure Determinants and Mechanisms

Spacecraft cells and batteries may be tested under three ideal electrical regimes (Table 17):

(1) Constant voltage
(2) Constant current
(3) Constant power

In any one practical application, however, not only may one or more of these regimes be used but the regulation may also be far from constant. In any test, the cycle period (time) will usually be fixed; therefore, if a cell or battery does not perform satisfactorily for the duration of the cycle, the failure mode can be described in terms of either voltage or current rather than time. Hence, in Table 17, only the voltage and current tolerances have been given as the variables of interest in failure analyses. Table 17 also gives the total number of possible failure modes associated with these variables. These six modes are the

Table 17—*List of possible failure modes for sealed spacecraft cells.*

Limiting or Test Application	Variable	Failure Mode	Description
Current	Voltage E	$+E_c$	Voltage too high on charge
		$-E_c$	Voltage too low on charge
		$-E_d$	Voltage too low on discharge
Voltage	Current i	$+i_c$	Current too high on charge
		$-i_c$	Current too low on charge
		$-i_d$	Current too low on discharge
Power	Voltage E and current i	$+i_c, -i_c$	Current too high or current too low on charge
		$+E_c, -E_c$	Voltage too high or voltage too low on charge
		$-i_d, -E_d$	Current or voltage too low on discharge

first tool for classifying data in a search for failure determinants and mechanisms.

The next step toward describing failure mechanisms is to identify the various determinants associated with each failure mode (Table 18). For controlled testing of cells or batteries with constant current or constant voltage, the determinants used to describe the $+E_c$ mode are the same as those for the $-i_c$ mode and, similarly, for the $-E_c$ and $+i_c$ modes and the $-E_d$ and $+i_d$ modes. Many of the determinants listed in Table 18 can be related to, or observed, as internal resistance changes. Observations associated with the $+E_c$ mode will usually show as excessive gas pressures, whereas for $-E_c$ and $-E_d$ a loss of capacity can be identified. With these simplifications in mind, it is possible to compile a list of failure determinants and mechanisms applicable to spacecraft

Table 18—*List of possible failure mechanisms associated with the determinants of the voltage or current failure mode.*

Failure Mode	Failure Determinant	Suggested Failure Mechanisms
(1) $+E_c$ or $-i_c$	Temporary or permanent passivation of electrodes	(a) Carbonate film buildup on surface of electrode due to increased CO_2 in electrolyte (b) Changes in crystallinity and porosity with cycling
(2) $+E_c$ or $-i_c$	Improper balance of active materials	(a) Improper charge balancing of elements
(3) $+E_c$ or $-i_c$	Electrolyte loss or composition change	(a) Loss from evaporation or spray due to faulty closures, including corrosion of the seals (b) Absorption of CO_2 from the air; degradation of the separator (i.e., soluble electrode materials reacting to give insoluble product, surfactants, or additives)
(4) $+E_c$ or $-i_c$	Change in properties of separator	(a) Increased resistance due to change in composition, porosity, or wettability
(5) $+E_c$ or $-i_c$	Corrosion of tabs, collectors, or terminals	(a) Reduction in cross-sectional area leading to increased cell resistance (b) Deterioration of contacts, welds, or grids, leading to increased cell resistance
(6) $-E_c$ or $+i_c$	Short circuit between electrodes	(a) Migration of negative electrode material and redeposition in separators (b) Extraneous material between electrodes, due to nickel-sinter corrosion or poor quality control (c) Degradation of separator, including "burning" and the effects of sterilization

Table 18—*Concluded.*

Failure Mode	Failure Determinant	Suggested Failure Mechanisms
(7) $-E_c$ or $+i_c$	Short circuit between electrodes and case	(*a*) Breakdown of insulating properties of seals (*b*) Excessive migration of active electrode materials; shape change (*c*) Auxiliary electrode tab touching other electrodes; poor quality control
(8) $-E_d$ or $+i_d$	Short circuit between electrodes	(*a*) Migration of negative electrode material and redeposition in separators (*b*) Extraneous material between electrodes due to nickel-sinter corrosion or poor quality control (*c*) Degradation of separator, including "burning" and the effects of sterilization
(9) $-E_d$ or $+i_c$	Short circuit between electrodes and case	(*a*) Breakdown of insulating properties of seals (*b*) Excessive migration of active electrode materials (*c*) Auxiliary electrode tab touching other electrodes; poor quality control
(10) $-E_d$ or $+i_d$	Loss of electrode capacity	(*a*) Memory effects, temporary or permanent passivation, drying out of positive electrodes, all leading to inefficient charging (*b*) Change in balance of active materials in electrodes (*c*) Spontaneous decomposition of active materials (*d*) Reduction of charged materials by hydrogen evolved due to corrosion or by soluble organic materials in electrolyte or reduced active material

cells and batteries which, properly interpreted, can be used to describe any failure mode.

Table 15 lists the suggested failure mechanisms for the determinants of the voltage or corresponding current failure modes, as deduced from information reported in the literature. Certain mechanisms (i.e., 2*a*, 6*b*, 7*c*, 8*b*, and 9*c*) are not time dependent in the sense that they might be monitored during an accelerated test. For example, mechanisms such as 7*c* and 9*c* might result from poor quality control and need not be considered as part of an ideal accelerated

test. The other mechanisms in Table 15 will change as some function of time and should, therefore, be related to stresses and strains in Table 12 for structuring an accelerated test. Note that because of the definitions given for an ideal accelerated test, the useful mechanisms for analysis of data are, by necessity, rate processes.

The most frequently reported determinants or mechanisms for all common types of sealed cells are as follows, in order of frequency of occurrence:

(1) Internal shorts
(2) Seal or case leaks
(3) Loss of capacity
(4) Migration of active materials
(5) Separator degradation
(6) Excessive gas pressures
(7) Tab faults
(8) Carbonation of electrolyte
(9) Cell imbalance

No effort was made to differentiate between failure determinants or mechanisms in making the tabulation. Some idea of the relative dominance of the failure determinants for nickel-cadmium batteries is given in Table 19, taken from Sparks (Reference 50). The numbers represent the failure rate times 10^{-9} per hour. It should be realized that the list and Table 19 are not totally unbiased, for two reasons. First, only data reported in available literature were used to compile the listings. Second, during life testing, and often during actual use, a temporary loss of capacity occurs. This loss is not reported because reconditioning of the cells (e.g., by capacity checks) erases the effect. Thus, the cell may eventually fail by internal shorting and be reported as such, even though reconditioning was necessary to restore the temporary loss of capacity.

Table 19—*Typical failure occurrences for nickel-cadmium cells.*

Failure Determinant	Years of Life					
	1	2	3	4	5	6
Plate-to-plate short	50	50	50	100	200	500
Terminal-to-case short:						
1-seal design	10	10	20	50	100	500
2-seal design	3	4	6	8	12	17
Seal, case leak	10	20	35	55	75	100
Cell imbalance	10	20	50	100	500	1000

In terms of an ideal test, then, the important failure determinants to be considered are—

(1) Plate-to-plate short circuits (determinant 6 in Table 18)
(2) Plate-to-case shorts for one-seal design or case-to-terminal shorts for two-seal-closure designs (determinant 7 in Table 18)
(3) Loss of plate capacity (determinant 10 in Table 18)

Migration of active materials and separator degradation are both included in the three determinants listed above.

Excessive gas pressures, which can cause cell bulging or rupture and, hence, electrolyte loss, are related to $+E_c$ and $-E_d$ and are influenced by such variables as ambient temperature, electrolyte level, and balance of active materials. If the cell voltage is adequately controlled and limited on charge or discharge, the problem of gas evolution and accumulation will not arise when there is enough excess negative-electrode capacity.

AN IDEAL PHYSICAL APPROACH TO ACCELERATED TESTING

The physical approach to accelerated testing developed in this report has not been put to practice. It is a conceptually ideal approach to the measurement of cell or battery qualities and the time or cycle rate of change of those qualities as a function of various stresses at different levels of intensity. From the viewpoint of physical chemistry, therefore, the ideal test program would be based on some understanding of the mechanisms causing failures such that the stresses and strains in Table 16 would be related to each failure mechanism. The equations in Table 15 would show the relevant variables to be measured and how these variables are to be dealt with. Interrelations between different stresses would be deduced on the basis of the conservation laws. Initial qualities (Q_I of Equation 10 or Q'_I of Equation 41) would be measured. Because only electrical qualities are associated with battery failures, only two qualities are necessary: voltage charge quality and voltage discharge quality. All stresses other than electrical would be related to the voltage quality Q_E. Then, the rate at which Q_E changes with number of cycles or time would be measured at high stress levels to allow an early prediction of failure at normal operating stress levels.

To illustrate how this ideal test might be applied, consider some of the failure determinants or mechanisms reported in the battery literature and listed in Table 18. Three are given as follows with the stresses to which they should be related (from Table 16):

(1) Internal shorts: related to concentration, temperature, and voltage gradients
(2) Seal or case leaks: related to pressure, temperature, and velocity (vibration) gradients
(3) Loss of capacity: related to concentration, voltage, and temperature gradients

In each example, temperature gradients appear to be a contributing factor to failure. Therefore, the relationships between temperature gradients and other stresses appear to be the most important considerations for development of accelerated tests.

Another important stress appears to be that of concentration gradient. Such a stress cannot be measured directly inside sealed cells. Therefore, accelerated test techniques must make use of other stresses and strains to control, vary, and measure, by inference, the concentration gradients.

SUMMARY OF PHYSICAL APPROACH

As shown in this section, an ideal physical approach to the accelerated testing of rechargeable cells requires an operational measure of the quality of a cell. It is suggested that the quality Q_I of a cell at a particular time within a charge-discharge cycle be defined as

$$Q_I = \frac{1}{\Delta In}$$

where ΔI is an observed intensity factor change at an hourly rate of charge or discharge n.

It is further shown, using stress/rate-of-strain relations, that the stresses acting on a cell are related to intensity gradients that are associated with changes of voltage, temperature, pressure, and concentration over some finite distances within cells. The relevant distances within cells are either fixed or unmeasurable; concentration gradients cannot be measured directly because the cells are sealed. Consequently, it is recommended that accelerated tests for cells should be set up and analyzed in terms of measurements of voltages, temperatures, and pressures. The initial qualities and the rates of degradation would be used to predict time to failure for any given cell.

Intensity gradients are found to be associated with the operating stresses on a cell and are measured in terms of voltage, pressure, and temperature variables for practical applications, as shown in Table 20.

The data requirements for a physical approach to an ideal accelerated test program for rechargeable cells are given in the following list. The voltage, temperature, and pressure measurements would be taken at the end of discharge and at the end of charge in each charge/discharge cycle. The voltage gradients would be varied in two ways: by five levels of strain and by five levels of rate of strain. The computation of qualities with their time rates of change would be easily accomplished by an offline computer.

(1) Cell weights and volumes (qualities converted to equal weights or sizes for intercomparison of cells with units such as mhos per cubic centimeter or mhos per gram)

(2) Cell length, width, and height (physical dimensions useful for estimating gradients)

Table 20—*Summary of important stresses and associated strains
applicable to rechargeable cells.*

Stress	Rate of Strain	Recommended Quantities
Pressure gradient	Volume flow per unit area	Q_P
Voltage gradient	Coulombs flow per unit area	Q_E
Temperature gradient	Calories flow per unit area	Q_T
Concentration gradient	Moles flow per unit area	None
Velocity gradient	Change of momentum per unit area	None
Frequency gradient	Photons absorbed per unit area	None

$$Q_P = \frac{\text{amperes}}{\Delta P \cdot \text{ampere-hours} \cdot \text{liters}/F} \ .$$

$$Q_E = \frac{\text{mho}}{\text{cubic centimeters}} \text{ or } \frac{\text{mho}}{\text{grams}} \ .$$

$$Q_T = \frac{\text{amperes}}{\Delta T \cdot \text{ampere-hours} \cdot \text{grams}/\text{ampere-hours} \cdot C_v} \ .$$

(3) Cell specific heats (calories per degree per gram) (for physically meaningful units of temperature qualities, convert Equation 10 into units such as amperes per calorie)

(4) Charge and discharge current (all tests made at constant current)

(5) Environmental temperature (all temperature changes in a cell measured relative to constant environmental temperatures)

(6) Cell ampere-hour capacities (cells being placed on life tests matched on the basis of equal ampere-hour capacities)

(7) Initial end-of-charge voltage (cells being placed on life tests matched on the basis of equal end-of-charge voltages; voltage changes (ΔV in Equation 10) measured relative to initial end-of-charge voltage)

(8) End-of-charge and end-of-discharge voltages at positive terminal versus third electrode and negative terminal versus third electrode, or positive and negative terminals (calculation of cell voltage qualities, Equation 10)

(9) End-of-charge and end-of-discharge temperatures at positive terminals and center of active materials on outside of case (calculation of temperature qualities with units such as amperes per calorie and for diagnostic purposes during subsequent failure analyses)

(10) End-of-charge and end-of-discharge pressures (calculation of pressure qualities with units such as amperes per liter per atmosphere for diagnostic purposes during subsequent failure analyses and for safety purposes by avoiding explosions or bursting cells)

A major accomplishment of the physical approach consists of the identification of stresses as intensity gradients. This single accomplishment allows a variety of complexities with spacecraft cells to be simply correlated with a vast body of accepted physical knowledge. A wide assortment of stresses and accelerated tests are thereby inferred. For example, the following can be seen from Table 18:

(1) Pressure gradients can be both static and dynamic. Static pressure gradients can exist across the cell case, between electrodes, or between pores of electrodes; dynamic pressure gradients can be associated with fluxes of moving materials, either solid, liquid, or gaseous. The way in which individual cells are retained in a battery of cells could be an important variable in connection with cell life as affected by pressure gradients.

(2) Voltage gradients will vary with depth of discharge, amount of overcharge, and rates of charge and discharge. Voltage gradients will depend also on cell and electrode dimensions, including areas and thicknesses. Thus, a cell designed for an initially high quality may not be well designed for long life. Voltage gradients may or may not have associated with them temperature gradients and concentration gradients; but if these additional gradients exist, there will be an increase in the rate of degradation of voltage qualities.

(3) Temperature gradients are always to be expected in operating spacecraft cells. If a test were to be designed so that absolutely uniform temperatures were to be retained throughout cells, there would be no temperature gradients and no temperature stress. Any effects of temperature would then be associated with the concentration, pressure, or voltage gradients brought about by the constant temperature level. Since uniform temperatures cannot be attained in actual tests, there will always be temperature gradients. These gradients should be directly proportional to the temperature differences in a cell because the physical dimensions of cells change very little. Hence, the rate of temperature changes and the relationships in columns 7, 9, and 10 of Table 15 could reveal degradation of cell qualities.

(4) Concentration gradients are never absent in sealed cells. Even in a completely discharged state, the negative electrodes are saturated with $Cd(OH)_2$ and the positive electrodes are saturated with $Ni(OH)_2$, which create concentration gradients. In the charged state, concentration gradients could be maximized. Soluble organics from the separator and other elements and compounds can provide concentration gradients that cannot be monitored but which can accelerate the degradation of quality.

(5) Velocity gradients can be associated with vibration tests. In general, a high-quality cell will show negligible electrical effects due to vibration. For spacecraft cells, vibration tests would be useful for acceptance specifications, but once the cells are in space, the effects of vibration should be negligible.

(6) Frequency gradients in Table 18 refer to adsorption of electromagnetic radiation. If there is negligible adsorption, there will be negligible stress and, hence, negligible effect on cell life.

6 HARDWARE CONSIDERATIONS

In specifying an experimental procedure in which batteries are to be subjected to accelerated tests and the results are observed, the problem of the adequacy of available hardware arises. Such hardware may be best discussed in three general categories. The first category involves the supply and controls necessary to charge and discharge the cells under test. These considerations include the programming controls that automatically put the cells through a selected schedule of cycles with automatic changes within any cycle. The second category of hardware involves the measurement of all variables deemed significant. The measurements must be selected in such a fashion that any of the analyses previously described in this report can be performed. The third category is concerned with instrumentation required to store and analyze the data generated during the cycle tests. These three categories are discussed separately; it will become apparent that some type of computer will be necessary to satisfy the requirements. A detailed list of equipment requirements is given in Appendix C.

TEST-CONTROL AND PROGRAMMING REQUIREMENTS

From the various concepts of the ideal accelerated tests previously presented, there exist some common requirements. All of these concepts are based upon some form of cyclic operation of the cells at various levels of stresses. Adequate ranges for the charging and discharging rates must be provided to insure that the stress levels are not limited by the power supplies. In addition, power supplies must be sufficiently stable to establish and maintain constant-current or constant-voltage modes of operation. Solid-state instrument technology incorporated in currently available power supplies is capable of excellent long-term use with adequate voltage and current ranges and controlled regulations to a few hundredths of a percent. However, the regulatory performance of these power supplies should be checked from time to time to insure constant-current or constant-voltage operation; the ripple content of the output should also be within the manufacturer's specifications.

Programming of the cycling regime of the cells may be accomplished with commercial programmers. However, the compiling of an online programmer with feedback computer control of the program parameters may require some

specialized electromechanical units to insure that the sequencing, synchronizing, and repeatability of the programming units do not introduce variations in the data.

MEASURING AND RECORDING TEST VARIABLES

Ideal accelerated tests require recordings of the performance of individual cells and groups of cells. Stress levels and operating conditions must be defined in terms of practical measurable quantities. Some quantities, which themselves are not easily or accurately measured, may be inferred by measuring related phenomena and then calculating the desired quantities from known relationships. For example, the thermal-energy content of a cell may be obtained from measurements of temperatures, specific heats, and masses of the various components. The adequacy of a temperature-gradient measurement is limited by the difficulty of locating a temperature sensor in the proper place. However, if some of the stress levels or performance phenomena cannot be measured or inferred with present techniques, they become the subject for needed research.

The recording of battery-performance parameters for accelerated tests presents two demands that are opposite in nature. On one hand, the changes that describe degradation in batteries over many cycles occur at a very slow rate. On the other hand, the changes in any one parameter, such as voltage, may show a rapid change during portions of an individual charge/discharge cycle. Hence, the recording demands vary from the need for a fast, continuous recording to those instances in which a single recording every few hours or every few days might be sufficient.

The recording rate of the required data system should not yield voluminous, redundant data when little or no change in the variables of interest are being observed. The frequency of measurement can be altered to insure efficient use of the equipment. Prior experience or good judgment can suggest the magnitude of changes in the variables which may be of value to the analysis and subsequent predictions. These changes can be used with an online control/acquisition computer. In such a test, the data are continuously scanned, but only changes equal to or greater than those of interest are recorded.

Operating Ranges of Instrumentation

The range of operating conditions for the cells on test depends on three basic factors. First, the ampere-hour capacity of the cell will help determine the current ranges if fixed rates of charge or discharge are selected. Second, for any given cell-capacity size, the choice of the highest and the lowest stress levels will set the upper and lower limits for certain variables, such as voltage or current. Third, the available equipment and the relative cost and power

requirements of the test facility can influence the range of operating conditions finally selected.

General recommendations for testing nickel-cadmium cells are as follows:

(1) The voltage range anticipated for each cell will be between 0 and 2 V. This range is within the scope of commercially available instrumentation.

(2) The voltage range anticipated for each matched group (see Section 7) of 10 cells will be between 0 and 20 V; thus, an instrument capable of measuring 0 to 20 V full scale will be suitable.

(3) Controlled temperature facilities should be available to test batteries between the common military specifications of about 213 to 343 K ($-60°$ to $+70°$ C). For sealed nickel-cadmium batteries, ambient temperatures should be controlled between the lower and upper limits of 243 and 323 K ($-30°$ and $+50°$ C), for purely practical reasons. That is, below 243 K ($-30°$ C), the reaction kinetics are slow enough and polarization losses are relatively large enough that the nickel-cadmium battery is not expected to deliver the desired power. Above 323 K ($+50°$ C) the rate of self-discharge, chemically and electrochemically, is relatively fast enough that maintenance of charge may be difficult. Within this temperature range, the degradation mechanisms leading to failure are expected to be reasonably stable so that the accelerated life test data are valid.

(4) The current range of the instrumentation for matched groups of 10 cells will vary according to such factors as cell size and depth and rate of discharge. However, an instrument with variable ranges from 0 to 200 A should satisfy the test requirements.

(5) The pressure range anticipated should be detectable with a gage reading between 0 and 1400 kN-m^{-2} (200 psig). A variable bias to shift the zero point is recommended.

These operating ranges are also compatible with the testing of silver-zinc cells because the cell voltages lie between 0 and 2.0 V. It is anticipated that cells of ampere-hour capacities similar to those of nickel-cadmium cells will be tested; if larger ampere-hour capacity cells are used, different current ranges on the equipment may be used, but an instrument with a range from 0 to 200 A should still be suitable.

Stability and Precision of Instrumentation

Equipment adequate to control the tests at any desired point within the desired combinations of the maximum ranges stated above should be chosen on the basis of good resolution of control settings and on the basis of stability of set values over long periods of time. The stability of set values of test conditions should be measured rather than assumed. Portions of the data

Table 21—Guide to instrument selection for use in battery testing.

Quantity To Be Measured	Type of Instrument Used	Recommended Ranges and Impedance[a]	Type of Outputs Available	Nominal Speeds of Response	Recommended Accuracy (percent of full scale)
Closed-circuit terminal voltage	Voltmeter: Indicating	1000 Ω/V	Visual	Hundredths of a second	0.5
	Digital	1-10 MΩ	Visual and code	Several points per second	0.1
	Potentiometric	200 000 Ω and higher	Record and code	1/2 s	0.25
Open-circuit terminal voltage	Voltmeter: Indicating	200 000 Ω/V	Visual	Hundredths of a second	0.25
	Digital	1-10 MΩ	Visual and code	Several points per second	0.1
	Potentiometric	200 000 Ω and higher	Record and code	1/2 s	0.25
	Differential	VTVM 1-10 MΩ	Visual and analog record	Manual	0.01
Current	Ammeter: D'Arsonval	Maximum current rating	Visual	Hundredths of a second	0.5
	Shunt	Maximum current rating	Millivolts recorded	Continuous	0.1
Capacity	Ammeters and clocks	Maximum current rating	Visual	Continuous	0.25
	Ampere-hour meter	Maximum current rating	Electromechanical counters with visual or coded output		0.25
	Ampere-minute meter Coulometer Coulometer	Maximum current rating			
Pressure	Gages	-100 to 1400 kN·m^{-2} (-15 to +200 psi) for Ni-Cd batteries	Visual	Not critical	0.25
					1.0
	Transducers	-100 to 1400 kN·m^{-2} (-15 to +200 psi) for Ni-Cd batteries	Electrical analog		1.0
Temperature	Thermocouples:	Reference junctions			
	Millivolt meters	Low impedance	Visual and recording analog	Manual or automatic, continuous	0.5
					0.25
	Digital meters	High impedance	Visual and recording digital	Intermittent, several points per second	0.10

[a] All readings should be in upper half of scale.

system should be devoted to monitoring these values in order to establish the stability of the test conditions. Variations in the set test conditions should be known to an accuracy at least as high as that desired in the test data being generated and recorded. Also, variations in the test conditions (noise) should be small with respect to the variations in cell performance (signal) to avoid interpreting the effect of test condition changes on cell performance changes.

A digital voltmeter with an accuracy of ±1 mV will be necessary. The combined requirements of 2.0- or 20-V full scale with readings to ±1 mV make it important to know the way in which voltmeter specifications are written. For example, a typical specification for the accuracy of a digital voltmeter might be 0.01 percent of reading, ±0.005 percent of full scale, ±1 digit, at 298 K (25° C). Hence to be sure of 0.1-percent accuracy in the readout to the nearest millivolt, an instrument with an accuracy of 0.01 percent is required with a six-decimal-place display and a five-decimal-place recording capability.

Bauer (Reference 51) discusses further the problem of accuracy of measurement in the testing of cells and the maintenance of measurement standards; some practical secondary standards for the detection and correction of instrument drift are—

(1) Voltage: mercury cell in controlled temperature box; temperature-compensated zener diode.

(2) Current: precision power supply operating through a shunt with appropriate heat sink arrangements.

(3) Temperature: thermocouple with both junctions at controlled temperature.

Linebrink, Semones, and McCallum discuss instrument selection, ranges, and accuracies in a report on measurements of quantities which change in battery performance (Reference 52). This report, which is compatible with Reference 51, has been used to determine the accuracies specified for the electrical experiments. Table 21, taken from Reference 52, summarizes some of the factors governing instrument selection for battery testing.

AN IDEALIZED COMPUTER SYSTEM FOR DATA ANALYSIS

As indicated in previous sections, an ideal accelerated test for spacecraft cells would permit three kinds of data analysis: empirical, statistical, and physical. Empirical analysis is initiated online, serves as an initial filter for the detection of errors, makes tentative classifications of the raw data, and generally processes the accumulated data by a sequence of procedures designed to exploit selected structures detected in the data. Statistical analysis is initiated after the collection of a batch of data and is generally based on the assessment of the statistical significance, precision, and confidence levels associated with various averages and correlations. Special emphasis is given to those quantities that indicate the possible persistence of time-based trends found in the data. Physical analysis of data can be initiated online to compute initial qualities and to show their time rate of degradation.

Software for Empirical Analysis

The empirical approach requires an assortment of software packages that permit the generation of a wide variety of multivariate combinatorial classifications over time. New classifications must be generated, as warranted, by the data structures observed in prior classifications. The output format required for empirical analysis consists primarily of frequency histograms, tables, and graphical displays of measured values. In general, the data-processing requirements are mathematically primitive because classifications are emphasized. However, storage requirements are created by the large number of measurements that must be processed. Additional requirements are created by the desire for a completely flexible online interaction with the data acquisition, handling, and reporting system. It appears that some recently developed software may permit the interactive capabilities required by the empirical analyst (References 53 and 54). However, the need for specific, empirically oriented software for data analysis is acute. Considerable software development appears to be required in this area to obtain a wide variety of mutually compatible programs that may be implemented in any sequence found appropriate for online interaction with the raw data.

Software for Statistical Analysis

The ever-increasing availability of statistical software suggests that standard programs are available from many sources for analysis of accelerated test data. Some ad hoc programming may be required to obtain statistical assessments of unusual data structures detected by empirical methods; however, these needs can be anticipated only when all causes of unusual data structure are understood from a physical process viewpoint.

In contrast to the online interactive requirements of the initial empirical analyses, the statistical programs generally suffice with batch modes of operation. Ideally, such batch analyses would be made during time that is available for use by the same computer system used for data acquisition.

Software for Physical Analysis

Software packages for physical analysis of accelerated test data are virtually nonexistent. One program developed by NASA and based on dimensional analysis may be particularly useful (References 55 and 56), but standard programs based on the Arrhenius or Eyring models, for example, do not appear to exist. In general, it may be premature to develop such software for routine application until a better understanding is obtained of the physical mechanisms associated with degradation of cells over time. Once the physical mechanisms and their associated laws are established, little difficulty would be expected in developing programs for the physical analysis of accelerated test data.

COMPUTER REQUIREMENTS

The test facility should have sufficient computer capability to permit the automatic charge/discharge cycling of the cells on test and the necessary online and the offline computer functions to be performed, including data processing and analysis. The requirements are discussed below; specific requirements are a 16 000-word memory for online operation and a 32 000-word memory for offline operation coupled with a 16-bit word and a scanning rate of 5000 measurements in 150 ms.

Online Computer Requirements

The online computer should carry out the program for data acquisition and the program for alarms. Control of the cycling experiments should be accomplished by independent equipment in case of online computer failure or downtime. The experiments should be stopped if the independent equipment fails but should not be stopped if a cell fails.

A scanner capable of taking 5000 measurements in 150 ms should be used in the data input systems. To permit some editing and tagging of data for subsequent analysis in an offline computer, a 16 000-word memory capability is recommended for the online computer.

Offline Computer Requirements

The offline computer should have the capability of running standard statistical programs (such as AID) and programs for regression analysis. A medium-sized scientific computer using Fortran IV language and having a memory of 32 000 words is recommended. This computer need not be a part of the test facility but should be conveniently accessible, with good staff coordination on efforts involving programming and data format.

7 REQUIREMENTS FOR THE EXPERIMENTAL DESIGN

The purpose of the experimental design consists of specifying the test conditions, the number of cells to be tested, the number of test conditions to be used, the type and amount of data to be generated, the methods of data analysis to be used, and the methods to be used for interpreting the results. The experiments that result from this design will yield information on the performance of the cells over a range of operating conditions so that predictions of performance can be made for operating conditions different from those specifically tested.

All data obtained are to receive an empirical analysis, but the experimental design will be based on a combination of statistical and physical considerations thought to be pertinent to the outcome of the tests.

EMPIRICAL APPROACH

Empirical methods of data analysis that have yielded good predictions of failure for cells in the QEL tests should be utilized whenever possible. These methods serve as a primary example of an empirical or cryptanalytic approach to data analysis. Some of the details for three indicators are summarized for easy reference.

In initial work on NASA battery test data analysis (Reference 57), indicators were developed on the basis of histograms made from frequency counts of voltage differences for 10 cycles of data per histogram. These indicators, although simple in concept, resulted in extremely good predictions of cell failure. The few cases where they produced poor predictions were traceable to bad input data or noise from the analog to digital converters. The initial input data consist of 5 to 10 charge/discharge voltage graphs, as diagrammed in Figure 15.

The ΔV's are measured in 10 increments from 0 to 0.09 V. Measurements above 0.09 V are classified as being equivalent to 0.09 V. A histogram is made from the observed frequency of occurrence of the ΔV measurements, counting each occurrence throughout the 5 to 10 cycles of data measured, as illustrated in Figure 16. Cells that failed early showed a pattern like that in Figure 17; cells that did not fail showed a pattern like that in Figure 18.

With appropriate weights assigned to the counts at different levels, the sensitivity to these various patterns can be amplified. Several patterns were
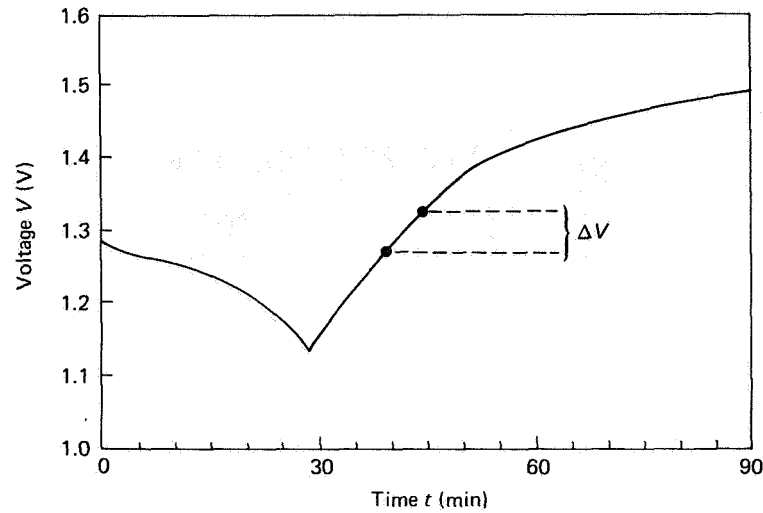
Figure 15—Charge/discharge voltage graph.
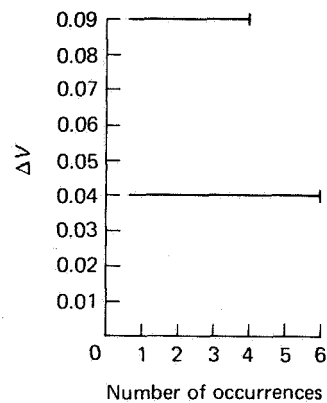
Figure 16—Typical histogram of frequency
of occurrence of ΔV measurements.
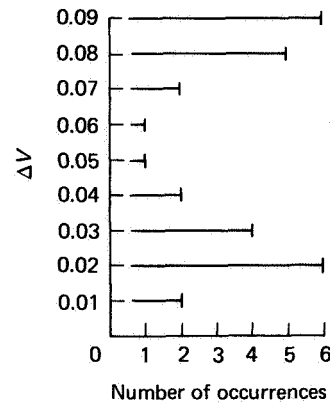
Figure 17—Typical histogram for
failed cells.

discovered to be very reliable in predicting cell failure or nonfailure and were therefore described as indicators. Although many indicators were tried, four particular indicators when taken together identified all the failures; three of these indicators are described.

(1) A pattern of relatively high frequencies of occurrence of 0.09-V differences is represented in Figure 17; cells failing with this particular indicator appear to fall into two categories: (a) high voltage at end of charge, and cell overcharging; and (b) low voltage at end of discharge, and loss of capacity.

Figure 18—Typical histogram for cells that did not fail.

Figure 19—Histogram of indicator no. 3.

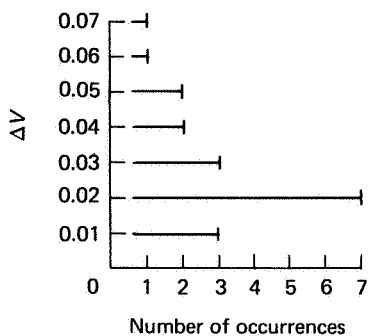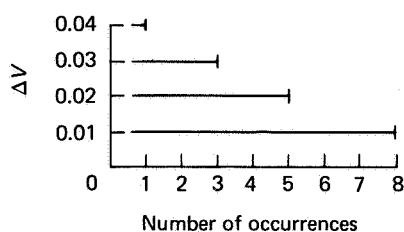(2) A pattern of relatively high frequencies of occurrence of 0.04- and 0.06-V differences was discovered by a computer gaming program. The cause is not clearly understood, but the appearance of this pattern always meant a negative prognosis.

(3) A pattern of relatively high frequencies of occurrence of 0.4- and 0.6-V differences (Figure 19) was observed in cells that lost electrolyte and weight. These cells would not accept charge; the 0-V difference always began to appear at a time corresponding to the end of charge.

In general, these indicators were discovered on the basis of QEL data only, which were cycled on a fixed regime and did not have maximum control in timing pulses for initiating measurements of voltage. The results could be improved for cell life prediction by designing a test system with these controls. Some data were analyzed with accurate readings every minute, and the information content of such data was not lost. Detailed descriptions of these indicators and others are reported elsewhere (Reference 58).

THE STATISTICAL APPROACH

Consideration will first be given to a complete factorial experimental design. The number of test conditions to be used depends on which of the following variables provide stresses that jointly affect the time rate of change of voltage quality in a quantitatively known, or unknown, manner:

(1) Environmental temperature

(2) Rate of change of environmental temperature

(3) Depth of discharge
(4) Rate of discharge
(5) Amount of overcharge
(6) Rate of overcharge
(7) Internal gas pressure or external retaining pressure
(8) Rate of generation or decrease of internal pressure
(9) Amplitude and frequency of vibration
(10) Electromagnetic radiation

Let S denote the number of stresses an electrochemist associates with the variables listed above and explained in Section 8. Five levels must be chosen for each of the stresses. Thus, for example, if two stresses are identified by the electrochemist, with five levels for the first stress and five levels for the second stress, there results a total of 25 combinations of stress levels. In general, the number of test combinations is given by 5^S. Three levels of each stress are required to determine whether the dominant failure mechanism changes over the range of the test conditions. An additional two levels are required so that if a change in mechanism occurs, it may still be possible to estimate the rate of degradation of quality over a more restricted range of operating conditions.

The required number of cells, then, is given by

$$N = 10(5^S) + 5S ,\qquad(61)$$

where the factor 10 denotes the 10 (replicate) cells to be used at each test condition. (The replicate cells are used for determining experimental error and for tear-down analyses during the test.) The term $5S$ denotes the number of cells to be subjected to a tear-down analysis prior to testing in order to establish initial characteristics.

Table 22 shows the required number of cells when the number of stresses varies between one and four. If more than four stresses are involved, an accelerated test should not be implemented until further laboratory studies determine which of these may be suppressed within reduced ranges of operation.

Table 22—*Number of cells required for accelerated testing using a complete factorial experiment.*

Number of Stresses S	Number of Combinations L^S of Stress Levels L Required	Number of Identical Cells R Required at Each Combination of Stress Levels	Number of Cells C for Initial Tear-Down Analyses	Total Number of Cells Required N
1	5	10	5	55
2	25	10	10	260
3	125	10	15	2165
4	625	10	20	6270

In column 1 of Table 22, the number of stresses is identified from the previously tabulated 10 conditions associated with degradation of quality. Only those stresses are used which dominate in some specified range of the experimental conditions; when more than two stresses are involved, a statistical response surface technique must be utilized.

In column 2, a minimum of five stress levels is necessary for each kind of stress because three stress levels are required in order to determine subsequently whether the dominant failure mechanism changed over the range of operating conditions. An additional two stress levels are required so that if a change of mechanism is indicated, it still may be possible to estimate a valid rate of degradation of quality over a more restricted range of operating conditions.

In column 3, 10 cells at each stress level are recommended so that at five successive times during the test a cell may be removed and subjected to tear-down or failure analysis. With this plan, the five remaining cells are expected to complete the test at each stress level.

In column 4, five cells for each selected stress are necessary to provide a statistically adequate control or reference base against which subsequent comparisons can be made. The number of cells constituting the control increases with the size of the experiment in conformity with the desire that the properties of the control be firmly established so that many comparisons may be made without losing statistical validity.

The final column is obtained from the relationship

$$N = L^S R + C, \tag{62}$$

with $L = 5, R = 10, C = 5S$, and $S = 1, 2, 3$, or 4, which is Equation 61.

When the chosen independent variables can be related to stresses and when the dominant failure mechanism is known, the physical approach should be used. When the failure mechanism involves two or more stresses in an unknown manner, electrical qualities should be plotted with polynomial functions into a response surface, as explained in Section 4.

PHYSICAL APPROACH

Electrochemists should identify which of the four specific stresses controls the dominant failure mechanism under intended-use conditions; i.e., gradients of pressure, temperature, voltage, or concentration. The means for creating this controlling stress will then be identified with 1 of the 10 variables listed under the statistical approach. It is anticipated that the independent variables 1 and 3 to 6 will cover substantially all of the known failure mechanisms; therefore, five distinct accelerated life tests are given in Section 8. Only one of these five recommended tests should be necessary, but two or more of them may be used in place of a factorial design experiment. Five examples are given with each test program to illustrate how a single test program might be selected.

It is believed that electrochemists know or can learn enough about failure mechanisms associated with spacecraft batteries to permit a proper choice of one test program per cell type per manufacturer. The following experimental design includes safeguards against improper choices so that a valid accelerated life test will be obtained. These safeguards include (1) two extra stress levels for extrapolation beyond an absolute minimum of three levels to validate a linear relation; (2) destructive tests to verify predicted failure mechanisms with actual observations; (3) a statistical response surface treatment of qualities, which does not require knowledge of physical mechanism; and (4) an empirical analysis of data with previously identified failure indicators, which can also help to provide a valid accelerated life test.

As an aid in identification of the dominant stresses and in selection of the experimental conditions, the following steps are recommended:

(1) Assume that all aging processes in sealed spacecraft cells will involve the physical movement or restructuring of matter, either active or inactive materials.

(2) Recognize that the movement or rearrangement of matter is a tangible manifestation of one or more of the identified, but intangible, stresses (i.e., gradients of temperature, pressure, concentration, and voltage).

(3) Select by experience, deduce from the literature, or based on available evidence determine which of the four stresses dominates the rate at which the movement, or rearrangement, of matter affects the electrical quality under intended end-use conditions.

(4) Select one of the independent variables, and identify the maximum value for that variable for which the dominant stress controls the failure mechanism.

At the present state of the art, the magnitude of acceleration factors cannot be predicted. However, when valid acceleration factors become available, fewer than the recommended 55 cells will be necessary for each accelerated test. Only six cells will be necessary to provide statistical significance to a single test at one stress level having a known and valid acceleration factor; i.e., one cell for initial tear-down analysis to show that the test cells are within standard errors of the values established by previous tests on identical cells plus five cells in the extreme valid accelerated test condition. A minimum of one cell will be necessary to predict life when the mechanism of failure and acceleration factor are completely known and generally accepted.

The selection of the controlling stress is important for a valid accelerated life test, but because of the safeguards itemized above, the selection is not critical. However, from a physical point of view, it is essential to identify a single controlling stress and a range of conditions where the associated failure mechanism dominates, if a valid accelerated test is to be attained in minimum time with the minimum number of cells. The five examples given with each test program in Section 8 will help illustrate how stresses, strains, and strain rates

are to be identified. To illustrate further the procedure for identifying the controlling stress, consider variables 1 and 3: environmental temperature and depth of discharge. Electrochemists will recognize that both of these variables could affect internal gradients of temperature, voltage, concentration, or pressure. In fact, any experimental variable may affect all known kinds of stresses in either a known or an unknown way. The electrochemist should perceive, however, that as long as one stress dominates the failure mechanism, any means for increasing that stress will increase the controlling degradation rate. Thus, in the chosen illustration with two variables, the electrochemist may know that the expected failure determinant for a given application will be internal shorts. He may know further that the mechanism for internal shorting is controlled by the stress of concentration gradients. Moreover, he may suggest that the concentration gradients may be controlled at different levels by using different levels of environmental temperature, by using different depths of discharge, or by both methods. The two chosen variables, temperature and depth of discharge, will yield different concentration gradients if each is varied separately; simultaneous variations in both variables undoubtedly will yield additional values of the dominating chemical stress. In any event, voltage qualities may be measured at five different pairs of temperature/depth-of-discharge conditions, including the intended-use condition. Extrapolations of quality versus time, or number of cycles, will then yield a valid prediction of life at each stress level if the time function is known. If quality is a linear function of time, the data may appear as shown in Figure 20.

If the electrochemist chooses to study each of the variables independently, he can expect to achieve a physically significant extrapolation by plotting rates of degradation of quality against the independent variable. Two experiments are then set up, with environmental temperature as the independent variable in one and depth of discharge as the independent variable in the other. If the concentration gradient is assumed to be the controlling stress for each experiment, both experiments will yield valid accelerated life tests with an
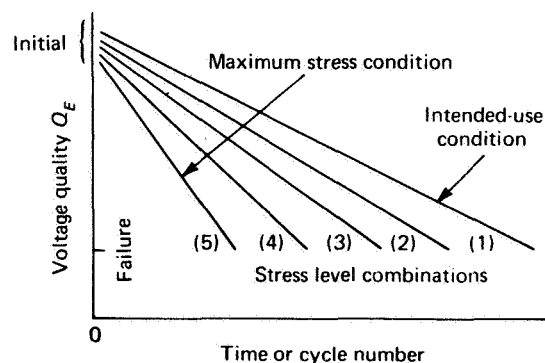

Figure 20—Voltage quality Q_E as a linear function of time.

easily determined extrapolation between the levels of each independent variable. However, the maximum acceleration factor will probably differ in the two experiments, and each acceleration factor will be less than the maximum acceleration factor obtained in an experiment that changes both environmental temperature and depth of discharge to levels different from their intended-use levels.

If the electrochemist anticipates that the intended-use condition may involve a number of variables over a range of values such that the failure mechanism differs during the lifetime of the cell, he should identify the two or more controlling stresses that correspond to the differing failure mechanisms. The electrochemist then has a choice of selecting either one independent variable varied over two different ranges or some combination of the 10 variables. If he chooses one variable to vary over the two ranges associated with the two failure mechanisms, he will achieve both a valid accelerated life test and a physically significant extrapolation by obtaining rates of degradation of quality at five levels within each of the two ranges. He may not achieve a very large acceleration factor, because all remaining variables are set at their intended-use condition. On the other hand, if the electrochemist chooses two or more independent variables that differ from the intended-use conditions, he will probably achieve larger acceleration factors. These results would then be utilized empirically to predict life at normal use conditions. Alternatively, techniques might be deduced for the direct measurement of concentration gradients at each test condition. Then, measured electrical qualities are plotted as an appropriate function of the concentration gradient. The number of independent variables changed simultaneously then makes no difference, provided that one test condition reproduces the intended-use value of all the variables associated with the intended-use concentration gradients.

In any event, the physical approach to accelerated life tests requires that only five cells be used for initial tear-down analysis. Thus, the number of cells in column 4 of Table 21 is constant at five, regardless of the number of stresses involved in the failure mechanism. Moreover, the physical approach allows a combination of two or more independent test programs to be performed on the same, nominally identical cells, but for different purposes. Then, the maximum number of cells becomes $50P + 5$, where P is the number of independent test programs selected from among those recommended in Section 8.

8 TEST PROCEDURE

IDENTIFICATION OF CELLS

The cells to be put on test should be fully identified as described below. Much of the necessary information is readily available and is usually supplied by the manufacturer or vendor. In an effort to obtain additional data that may have some relevance to understanding cell failures, Goddard Space Flight Center is introducing specifications (References 59 to 61) calling for specific information to be documented and supplied with each batch of cells. If possible, this additional information should be made available to the test program.

For the purposes of an accelerated life test, the following information is desired for full identification of a given cell. Only items 2, 3, 7, 8, 20, and 21 are essential for an accelerated life test program and must be provided to, or be determined by, personnel setting up the test:

    (1) Cell manufacturer

    (2) Cell type

    (3) Cell nominal ampere-hour capacity

    (4) Cell lot number

    (5) Date of sealing of cell

    (6) Cell identification number

    (7) Cell weight

    (8) Cell dimensions

    (9) Manufacturer's last measured ampere-hour capacity

  (10) Use history between date of cell sealing and date of receipt by purchaser

  (11) Type and number of positive plates

  (12) Type and number of negative plates

  (13) Type, separator, and method of plate wrapping

  (14) Concentration of electrolyte

  (15) Type of additions to electrolyte, if any

  (16) Volume of electrolyte added

  (17) Formation history of plates

  (18) Type of atmosphere within cell

  (19) Type of terminal insulation

(20) Type and function of auxiliary electrodes, if any
(21) Performance data and operating ranges for auxiliary electrodes as provided by manufacturer, if applicable
(22) Operating ranges recommended for cell
(23) Storage procedures recommended for cell
(24) Cell conditioning procedures

The cell's nominal ampere-hour capacity (3) is the capacity rating given by the manufacturer. Because spacecraft cells usually have built-in excess capacity, it is helpful to know the last measured ampere-hour capacity (9). The date the cell was sealed (5) is important because it is the basis of the definition given for the age of the cells (see Appendix B). The cell identification number (6) is that assigned by the manufacturer; if a number has not been assigned by the manufacturer, or if the number causes ambiguity, a life-test number should be given to the cell. Although items 22 through 24 do not identify the cell, the information may help to insure that the cell in no way is subjected to abuse before the life test begins. The information given by items 22 through 24 will help to enable an efficient test program to be set up and will also be of assistance in setting the requirements for the initial electrical examination of the cells.

INITIAL EXAMINATION OF CELLS

Acceptance Tests

Before being placed on the accelerated life test, each cell should be subjected to a thorough examination to insure that the purchase or acceptance specifications are met. The procedures and the results of these acceptance tests are included in the reports issuing from the "Evaluation Program for Secondary Spacecraft Cells" (NASA Battery Evaluation Program, Contracts W11,252B and W12,397). These publications, and the discussion given by Bauer (Reference 51) on acceptance testing, describe the tests that are presumed to have been done before the accelerated test program is selected.

Visual and Electrical Examinations

Before cell matching, the following initial tests are recommended for each cell:

(1) A visual inspection of the complete cell, including welds, seals, insulators, and so on
(2) A test for electrolyte leakage before and after cleaning and drying
(3) A determination of the cell weight (after cleaning and drying) to the nearest 0.1 g
(4) A determination of the dimensions of the cell
(5) An internal resistance (or impedance) determination to detect short or open circuits

(6) A test to check charge retention

(7) An X-ray examination of the cell to detect internal defects

It should be noted that these examinations are made to insure that the initial quality requirements set by the purchaser, or user, are met. These examinations are not designed to determine if the life requirements of the cell will be met.

CELL CONDITIONING AND MATCHING

The cells to be tested under each kind of stress should be electrically matched to obtain five relatively homogeneous groups with 10 matched cells in each group. One matched group of 10 cells is to be used at each of the five chosen stress levels. Five cells is the minimum number of replicates deemed necessary to provide statistically useful data. An additional five cells are provided for failure and tear-down analysis at parametric and operational failure times described in Section 9.

After the initial examination, the cells should be conditioned according to the manufacturer's recommended procedure. If no conditioning procedure is recommended by the manufacturer, it should be done in a manner compatible with the type and size of cell; References 17, 18, and 23 provide examples.

After conditioning, the cells should be subjected to three charge/discharge cycles for matching. Charging should be done at the $C/5$ rate for 7 hr, followed by a $C/2$ discharge to 1.0 V. The end-of-charge voltage and the discharge capacity, both measured during the third cycle, should be used as the basis for cell matching. These measurements should be used to sort the cells into preliminary groups of 50 or 75 for each stress to be utilized in the accelerated life test. Fifty cells are selected if 10 cells are to be used at each of five stress levels; 75 cells are selected if pressures are to be monitored in addition to voltages and temperatures. From the original lot of cells, five should be randomly selected for initial tear-down analysis.

Final matching of the cells into groups of 10 for each stress level shall be made on the basis of the most closely grouped end-of-charge voltages and discharge capacities within each preliminary group of 50 or 75.

THERMAL STRESS TESTS

The thermal stress test program is intended for use when it is decided that environmental temperature, under intended-use conditions, is the variable most likely to cause the rate-controlling stress for the dominant failure mechanism. Changes in environmental temperature are expected to lead to the movement or rearrangement of matter through sequences similar to the following examples:

(1) Changes in environmental temperature cause changes in the solubilities of cell materials, which create concentration gradients (the rate-controlling stress) and lead to the migration of active material.

(2) Changes in environmental temperature cause expansion or contraction of cell materials according to their differing thermal coefficients of expansion, which leads to pressure gradients (the rate-controlling stress) and the movement of matter.

(3) Higher environmental temperature decreases charging efficiency at the positive electrode, which leads to internal gas pressure, which creates internal forces or pressure gradients (the rate-controlling stress) and the movement of matter.

(4) Lower environmental temperature decreases ionic mobility and diffusion rates, which create voltage gradients and the movement of charged material.

(5) Changes in environmental temperature create thermal gradients which cause the movement of matter by convection.

When environmental temperature is selected as the independent variable to generate stresses for a physically valid accelerated life test, five matched groups of cells should be tested. One group of 10 matched cells should be cycled at a normal (intended-use) temperature; the remaining four groups of matched cells should be tested at successively higher temperatures, with the last group of 10 matched cells operated at the highest temperature possible without changing the dominant failure mechanism of the cells. Charge and discharge strains and strain rates should be maintained at the intended-use condition.

A set of five matched groups of cells should be tested, with each group at a different environmental temperature in an environmental chamber. The five temperatures, controlled to within 0.5 K (0.5 C°), are selected as follows:

T_1: the lowest temperature, corresponding to the intended-use condition

T_5: the highest temperature, corresponding to the highest temperature believed not to change the dominant failure mechanism

T_2, T_3, T_4: the intermediate levels of temperature, chosen to be at equal intervals between T_1 and T_5 such that $T_1 < T_2 < T_3 < T_4 < T_5$ and $T_2 - T_1 = T_3 - T_2 = T_4 - T_3 = T_5 - T_4$

Every effort should be made to choose T_5 correctly; however, if the T_5-level subsequently appears to be too high because of a different degradation mechanism, the value of T_5 should not be changed, unless for example, the test facility is endangered by cell explosions. It would be preferable to generate data at the high level of T_5, but if T_5 is too high, predictions should be made on the basis of data obtained at temperature levels T_1 through T_4.

For the thermal stress tests, the intended-use conditions will determine the T_1 value. The rate of degradation and consideration of a change in the dominant failure mechanism will help determine a reasonable value for T_5. For example, the test range $T_5 - T_1$ for silver-zinc cells is larger than the same

range for nickel-cadmium cells because silver-zinc cells can be operated at higher temperatures. Thus, T_5 for nickel-cadmium cells should be set at about 323 K (50° C), whereas T_5 for silver-zinc cells should be set at about (343 K) 70° C (Reference 62), unless research shows the dominant failure mechanism at these temperatures to be different from the mechanisms at the lower temperature levels.

During the thermal stress tests, the charge and discharge strain and rate of strain should be maintained at the intended-use conditions. For a 20-A-hr nickel-cadmium cell, the charge strain might be 125-percent recharge if T_1 were 298 K (25° C), the discharge strain might be 25 percent, the charge strain rate might be 6.25 A, and the discharge strain rate 10 A for a 1.5-hr orbit period (Reference 63) with 30 min of discharge and 60 min of charge.

The voltage of the cell reaction is a function of temperature, and it is important to recognize that over the temperature range chosen in the tests, this voltage dependence will have some effect. Therefore, allowance for this effect should be made in setting voltage limits. For example, for a nickel-cadmium cell, the temperature coefficient of electromotive force (emf) has an average value of −0.000 45 V/K at 298 K (25° C). If T_5 were set at 323 K (50° C), the voltage correction at this temperature would be about 0.011 V, which is significant if voltages are being measured to the nearest millivolt. The average temperature coefficients of emf for silver-zinc and silver-cadmium cells are +0.000 22 and −0.000 35 V/K, respectively; allowance for these temperature coefficients of emf are the only temperature compensations needed for an accelerated life test of the type described here.

Cell temperatures should be measured during the tests in order that the thermal stress (temperature gradient) acting on each cell may be calculated. As a first approximation, overall temperature gradients may be calculated if the cell internal temperature, cell dimensions, and appropriate environmental temperatures are known. Because comparative values rather than absolute values are required, one particular cell direction may be chosen in order to calculate a single gradient for each cell. The direction recommended is from side to side, normal to the plane of the plates. It is not usually convenient to measure directly the internal temperature of a cell, but an indirect measure may be obtained from a measurement made on the positive terminal (Reference 51). Because of the good thermal conduction path between the cell interior and the terminals, the temperatures of the terminal and cell interior should not be substantially different (References 64 and 65). If a more accurate knowledge of the temperature gradients is required, the temperature of the cell case of the positive terminal should be measured. The cell-case temperature should be measured on a side face at a point corresponding to the center of the electrodes. (This will usually be about one-third of the way up from the cell-case bottom.) Note that, as before, the temperature measurement is made on the positive terminal. All temperature-measuring devices must be electrically isolated from other electrical circuits.

In thermal stress tests, it is possible that temperatures below the intended-use temperature may cause greater stress and accelerate the degradation of electrical quality. In this event, the five temperatures T_1 through T_5 should be chosen as before but with T_1 being the highest temperature (corresponding to the intended-use condition). Thus, T_5 would be the lowest temperature and would be limited in the extreme by the freezing point of the electrolyte of the particular cell type being tested. Temperatures T_2 through T_4 would be chosen, as before, to be at equal intervals between T_1 and T_5. Thus, if $T_1 = 298$ K ($+25°$ C) and $T_5 = 243$ K ($-30°$ C), then $T_2 = 284.25$ K ($+11.25°$ C), $T_3 = 270.5$ K ($-2.5°$ C), and $T_4 = 256.75$ K ($-16.25°$ C). The choice of whether to use increasing or decreasing temperatures to structure the thermal stress tests depends on the anticipated use of the batteries. Electrical qualities are to be monitored, as well as pressure or any other variable that can be related to the rate-controlling stress (i.e., gradients of temperature, voltage, concentration, or pressure).

ELECTRICAL STRESS TESTS

Four electrical stress tests may be structured according to whether (1) a stress-strain relationship or (2) a stress/rate-of-strain relationship is considered for the (3) charge or (4) discharge portions of each cycle. Thus, this section will describe a charge strain test, a discharge strain test, a charge strain-rate test, and a discharge strain-rate test. It is common practice to use depth of discharge or rate of discharge as the independent variables. However, depth of discharge and rate of discharge have been identified with strain and rate of strain, respectively, so that the setting of electrical stress levels for an accelerated test may tend to be an unacceptable procedure to electrochemists. Instead, the tests are designed with preselected strain and rate-of-strain conditions. Electrical qualities will then be monitored with cycling over real time. Simultaneously, the nonelectrical stresses, such as gradients of temperature, pressure, and concentration, are associated with the electrical strains and rates of strain and will affect degradation rates; therefore, changes in temperature, pressure, and concentration should be monitored when possible.

Test Procedures

Five matched groups of 10 cells should be used in each test program. One group of five matched cells should be operated under the intended-use conditions; the other four groups should be operated at successively higher strains or rates of strain such that the most severe operating condition is believed not to change the dominant failure mechanisms. Relative values are

$$S_1 < S_2 < S_3 < S_4 < S_5 \tag{63}$$

and

$$S_2 - S_1 = S_3 - S_2 = S_4 - S_3 = S_5 - S_4 \, , \tag{64}$$

where S_1 is the normal-use strain or rate of strain and S_5 is the highest strain or rate of strain believed not to change the dominant failure mechanism.

In these electrical stress test programs, the environmental temperature should be maintained at the intended-use temperature in an effort to minimize entry unwanted stresses into the program. The charging or discharging should be done in the constant-current mode. Where appropriate, voltage cutoffs should be used to change from high-rate charging to low-rate charging for the 4-hr cycle duration recommended.

Charge Strain Tests

The charge strain test program should be used when it is decided that under intended-use conditions and where environmental temperature will be relatively constant, failure mechanisms are most likely to occur during the charging portions of cycling. Overcharging is expected to lead to the movement or rearrangement of matter through sequences such as the following:

(1) Overcharging leads to oxygen evolution, which creates a concentration gradient through the separator and causes the movement of matter through oxidative reaction with the separator material.

(2) Carbon dioxide, created by a reaction similar to example 1, forms carbonate that can react with uncharged cadmium hydroxide at a rate controlled by concentration gradients of carbonate, thereby changing the negative active material into an inactive form.

(3) Overcharging leads to higher concentration gradients (the rate-controlling stress) and the corrosion of plaque materials.

(4) Charge strain leads to expansion of the positive active material, which causes that material to move or to pack into an inaccessible form.

(5) Overcharging, a strain, leads to oxygen evolution, which creates pressure gradients (the rate-controlling stress) and causes the movement of electrolyte, electrodes, cell walls, or other matter.

When a charge strain test is selected as the independent variable, five matched groups of cells should be tested using the percentage recharge as the strain for creating voltage stress. One group of 10 matched cells should be cycled at the normally intended percentage recharge; three groups of matched cells should be tested at successively higher percentages of recharge. The last group of 10 matched cells should be operated at the highest percentage recharge possible without causing a change in the dominant failure mechanism. The environmental temperature should be maintained at the intended-use temperature. The rate of recharge should be the same for all operating levels and should be determined by the normal-use conditions. (See "Charge Strain-Rate Tests" for an exception to the use of one rate of recharge.)

One group of 10 matched cells should be cycled at the normal intended percentage recharge. For example, for a 20-A-hr cell on a 1.5-hr-orbit (Reference 63), normal recharge might be 125 percent at a temperature of 298

K (25° C). The amount of recharge should be controlled to within ±0.25 percent, and the temperature should be controlled to within 0.5 K (0.5 C°). Three groups of cells should be cycled at successively higher percentages of recharge, whereas the last group should be operated at the highest percentage recharge possible without causing a change in the dominant failure mechanism. In the example given above, the normal charge strain is equivalent to 1 hr at 6.25 A. The maximum charge strain is estimated to be 9 hr at 6.25 A; the intermediate stress levels would then be selected at 3, 5, and 7 hr at the same 6.25-A rate. For the example given (Reference 63), the corresponding discharge strain might be 25 percent, and the discharge strain rate 10 A.

Discharge Strain Tests

The discharge strain test program should be used when it is decided that under intended-use conditions and where environmental temperature will be relatively constant, failure mechanisms are most likely to occur during the discharge portions of cycling. Discharge strains are expected to lead to the movement or rearrangement of matter through sequences similar to the following:

(1) Discharge leads to expansion (an increasing mechanical stress) of the negative active material, causing that material to move or to pack into an inaccessible form.

(2) Discharge leads to contraction of the positive active material, which causes that material to loosen where it is attached and move into an inaccessible position.

(3) As active materials move by reactions mentioned in examples 1 and 2, continued discharge cycles lead to concentration gradients (the rate-controlling stress) which degrade electrical qualities.

(4) Thermally insulated cells will heat during discharge in approximate proportion to the discharge strain, thus creating internal temperature gradients leading to increased solubilities and concentration gradients (the rate-controlling stress) and causing movements and restructuring of cell materials.

(5) Discharge strain leads to electrochemical polarization, which increases internal voltage gradients (the rate-controlling stress) and the movement of active materials present in ionized forms [e.g., $Cd(OH)_3^-$ or $Cd(OH)_4^{2-}$].

If a discharge strain test is selected as the independent variable, five matched groups of cells should be tested, with depth of discharge as the strain for creating electrical stress. One group of 10 matched cells should be cycled at a normal intended depth of discharge; three groups of matched cells should be tested at successively higher depths of discharge, but not exceeding 95 percent of the capacity measured when the cells were matched. The last group of 10

matched cells should be operated at the greatest depth of discharge possible without changing the dominant failure mechanism. The environmental temperature should be maintained at the intended-use temperature. A constant rate of discharge, determined by the intended-use conditions, should be used. (See "Discharge Strain-Rate Tests" below for an exception to the use of one rate of discharge.)

One group of 10 cells should be cycled at the normal intended depth of discharge, which, for example, for a 20-A-hr nickel-cadmium cell, might be 25 percent at 293 K (25°C) (Reference 63). The depth of discharge should be controlled to within ±0.25 percent, and the temperature should be controlled to within 0.5 K (0.5 C°). The next three groups of cells should be cycled at successively higher depths of discharge, and the last group of cells should be cycled at the greatest depth possible without changing the dominant failure mechanism. In the example given above, the maximum depth of discharge might be 100 percent; thus, the associated intermediate stress levels are set at 43.75, 62.5, and 81.75 percent. For all operating levels, the corresponding charge strain would be 125 percent, the charge strain rate 6.25 A, and the discharge strain rate 10 A.

Charge Strain-Rate Tests

The charge strain-rate test program may be used under two circumstances: when failure mechanisms are directly controlled by the charge rate because of the stresses associated with charge rates, and when failure mechanisms are independent of the charge rate but are directly related to the number of charge/discharge cycles. Failure mechanisms are expected to be controlled by charge rates through sequences such as the following:

(1) High charge rates lead to temperature gradients which cause mechanical stresses through expansion, contraction, and the movement of active materials.

(2) Temperature gradients created in example 1 cause migration of active materials.

(3) High charge rates lead to concentration gradients which enhance corrosion of the positive plates.

(4) High charge rates lead to voltage gradients which cause voltage-limit switching circuits to stop the charge current before active materials are fully charged.

(5) Voltage gradients resulting from reactions as in example 4 cause hydrogen evolution which, in turn, creates internal pressure, causing the cells to bulge, leak, or open at the seams.

When a charge strain-rate test is selected as the test program to accelerate the aging processes, five matched groups of cells should be tested, with the rate of charge as the rate of strain for creating a voltage stress. One group of 10

matched cells should be cycled at a normal intended charge rate. Three groups of cells should be tested at successively higher charge rates. The last group of 10 matched cells should be operated at the highest charge rate possible without changing the dominant failure mechanism. The environmental temperature should be maintained at the intended-use temperature. A fixed amount of recharge, determined by the intended-use conditions, should be used.

One group shall be cycled at the normal intended charge strain rate, which for example might be 6.25 A for a 20-A-hr cell at 298 K (25° C) (Reference 63). The charge strain rate should be controlled to within ±0.1 percent, and the temperature should be controlled to within 0.5 K (0.5 C°). Three groups of cells should be tested at successively higher charge rates, and the last group of cells should be tested at the highest rate possible without changing the dominant failure mechanisms. For the example chosen, the maximum charge rate might be 80 A; the associated intermediate stress levels should be set at about 24.7, 43.1, and 61.6 A. For all operating levels, the corresponding charge strain would be 125 percent, the discharge strain 25 percent, and the discharge strain rate 10 A.

The failure mechanism is sometimes independent of charging rate; advantage should be taken of this circumstance to achieve a maximum number of cycles in minimum real time. In this case, one of the other test programs is selected. At the maximum stress level for the selected test, a maximum charging rate again is chosen such that the failure mechanism remains unchanged. At the intermediate stress levels, intermediate charging rates are such that, at the normal (intended-use) stress level of the selected test, the cell is cycled at the normal charging rate. For example, one might run five depths of discharge from 100 to 25 percent, where 25 percent is the intended-use value. Since the intended use in the example also requires $C/2$ charging, the last group should be charged at $C/2$, whereas groups being discharged to greater depths may be charged at increasingly greater rates between $C/2$ and the maximum allowable rate.

Discharge Strain-Rate Tests

The discharge strain-rate test program may be used in two circumstances: when failure mechanisms are directly controlled by the discharge rate because of the stresses associated with discharge rates, and when failure mechanisms are independent of discharge rates but are directly related to the number of charge/discharge cycles. Failure mechanisms are expected to be controlled by discharge rates through sequences such as the following:

(1) High charge rates lead to temperature gradients which cause mechanical stresses through expansion, contraction, and the movement of active materials.

(2) Temperature gradients created in example 1 cause migration of active materials.

(3) High charge rates lead to concentration gradients which enhance corrosion of the positive plates.

(4) High discharge rates lead to voltage gradients which cause voltage-limit switching circuits to stop the discharging current before the discharge cycle has completed its required duration.

(5) Concentration or temperature gradients caused by high discharge rates may change the structure of active materials to a less active form.

(6) Higher discharge rates make current density distributions more uniform in electrodes such that life is increased rather than decreased.

This hypothetical effect of discharge rates is suggested because electroplating processes often tend to become more uniform at high current densities. If this beneficial effect of discharge rates were to occur in a significant amount, the effect should be taken into account in setting up the test program; however, discharge rate used as the main independent variable would then have doubtful utility because acceleration factors would be small.

When a series of increasing discharge strain rates is selected as the independent variable most suited for accelerating a known or assumed failure mechanism, five matched groups of cells should be tested. One group of 10 matched cells should be cycled at a normal intended-use rate of discharge. Three groups of matched cells should be tested at successively higher rates of discharge. The last group of 10 matched cells should be operated at the highest rate of discharge possible without changing the dominant failure mechanism. The environmental temperature should be maintained at the intended-use temperature. A fixed depth of discharge, determined by the normal-use conditions, should be used.

One group of 10 cells should be cycled at the intended-use discharge rate, which in the example chosen (Reference 63) is 10 A. This discharge strain rate should be controlled to within ± 0.1 percent. Three groups of cells shall be cycled at successively higher rates of discharge, and the last group of cells should be cycled at the highest rate possible without changing the dominant failure mechanism. If, for the given example, the highest rate were 90 A, the intermediate stress levels should be set at 30, 50, and 70 A. At all operating levels, the environmental temperature should be 298 ± 0.5 K $(25° \pm 0.5°$ C); the corresponding charge strain would be 125 percent, the discharge strain 25 percent, and the charge strain rate 6.25 A for the 90-min orbit.

In the second circumstance, failure mechanisms are independent of discharge rates but are dependent on the number of charge/discharge cycles; advantage should be taken of this situation so as to achieve a maximum number of cycles in minimum real time. Then, one of the other test programs is selected. At the maximum stress level for the selected test, a maximum allowable discharge rate is again chosen such that the failure mechanism remains unchanged. At the intermediate stress levels, intermediate discharge rates are also used such that at the intended-use stress level of the selected test, the cell is cycled at the intended-use discharging rate.

MEASUREMENT DATA TO BE RECORDED

Measurement data shall include the following at the beginning and at the end of each charge and at the beginning and at the end of each discharge:

(1) Real time
(2) Cycle number with symbol to denote charge and discharge portions of each cycle
(3) Current
(4) Environmental temperature
(5) Cell voltage
(6) Temperature at each positive cell terminal
(7) Pressure for appropriate cells (When considered important, cell pressure should be measured at each stress level on five extra matched cells having pressure transducers.)

In addition to the above reading times, temperatures (4), cell voltages (5), and pressures (7) should be measured at a rate determined by the scanner. Real-time and numerical values of voltages, temperatures, and pressures should be recorded as described below; real time should also be recorded whenever a change is made by means of an external control.

Amount of Data To Be Recorded

To obtain the frequency of measurements, it is recommended that the range between each value (voltage, pressure, temperature, and so forth) at the beginning of each experiment and the corresponding estimated final value be divided into 20 equal intervals for computer control. As each measurement of a variable is scanned, the value of the measurement would be classified into one of the 20 intervals and a continuously updated cumulative frequency count would be made of the number of measurements that fall in each of the intervals. A similar frequency count would be made for the computed values of electrical quality. Moreover, the real time of transition from one interval to another would be recorded. Cycle number may be used, provided the start of a cycle and elapsed time within a cycle are properly synchronized with real time.

Because initial cell quality is anticipated to degrade slowly over time (or cycle number), most of the early measurements are expected to fall into that interval associated with the highest quality. However, as a test progresses, cell quality is expected to degrade more rapidly, and the corresponding measurements will be classified into intervals associated with decreasing quality, and the transitions from one interval to the next will be made more rapidly. This nonlinearity is shown schematically in Figure 21 for a hypothetical rate of degradation of electrical quality. With a monotonously decreasing variable, this procedure will result in the recording of transition times when each 5-percent increment of degradation is first encountered.

The experimental variables to be recorded during an accelerated life test are categorized under four headings: identification data, cell group data, individual
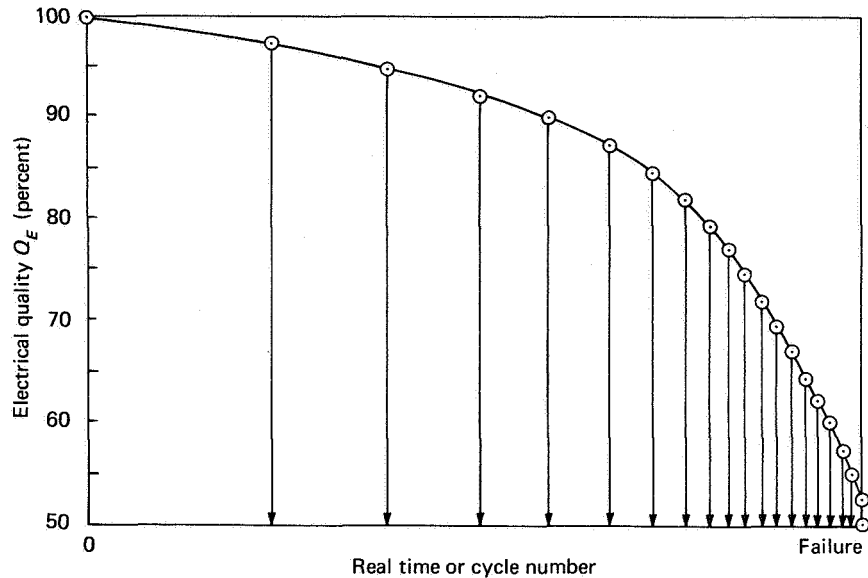
Figure 21—Schematic diagram showing expected transition times among 20 equal intervals of electrical quality as a function of real time or cycle number.

cell data, and control data. However, it does not necessarily follow that the scanner channels should be wired to record the data in this sequence. The exact scanning and recording sequence depends on the structure of each test program, the variables to be recorded, and the priority given to each piece of data recorded.

Identification Data

Identification data are necessary to identify the group of cells in each test and the time of each datum record. Thus, this information includes the cell group number, the cycle number, the real time of the start of scan to be recorded, the scan number at the beginning and end of each charge or discharge cycle, and the number of the recording scan. The cycle scan number and real-time record should be qualified by a symbol (such as C or D, or "+" or "−") to denote whether data are being recorded on the charge or discharge portions of that cycle.

Cell Group Data

The charging and discharging of the cells that are series connected in each matched group should be done at chosen constant-current levels. Group current should, therefore, be recorded and monitored along with a real-time record of such events as the changeover from a high-rate charge current to a low-rate charge current. For test programs other than the thermal stress tests,

the environmental temperature of the group should be measured at a chosen, representative spot within the environmental chamber.

Individual Cell Data

Each individual cell can be identified from the scanner channel number. Depending on the type of test being run, the variables will assume different relative importance. However, voltage and temperature data should be recorded for each individual cell. To avoid stray electrical signals, temperature-measuring circuitry must be isolated electrically from the cells. Pressure should be measured and recorded for those additional matched cells having pressure transducers, which may be optionally included in a test.

Control Data

The controlled parameter measurements will be recorded under all group and individual cell data; however, various other measurements should be recorded periodically (at least hourly) to monitor the operation of the test facility and the operation of the actual accelerated life test. These additional data recordings are comprised of the real time of each check made, voltage reference stability, temperature reference junction stability, power supply stability, and the real time of any changes made to the life test, with the changes being carefully documented.

Summary

Combining the inputs from the above recordings, a measurement data record should include the following:

(1) Scan number
(2) Real time at start of group scan
(3) Class interval in question
(4) Cell group number
(5) Cycle number and symbol
(6) Group current
(7) Group environmental temperature
(8) Elapsed real time within a cycle, and symbol
(9) Cell voltage
(10) Cell temperature
(11) Cell pressure, if appropriate
(12) Voltage reference check
(13) Temperature reference junction check
(14) Time synchronization check

9 PREDICTION OF PARAMETRIC FAILURES

The purpose of the analysis of the data consists of generating reliable predictions of cell life at intended-use conditions by means of data obtained at more severe operating conditions. To accomplish this purpose, the analysis should yield a reliable prediction of electrical quality over extended time periods as a function of stress level, cell history prior to initiation of test, and performance observed over short time periods during the test. The analysis should also yield predictions of performance for operating conditions between those specifically tested. Empirical, statistical, and physical methods of data analysis are used to ensure that maximum predictive information is obtained from the data.

Sections 3, 4, and 5 serve as the basis for developing these methods of data analysis. Also, Reference 1 discusses in detail other methods of analysis, which, although not specifically recommended for the present test program, could be used to analyze the test data to supply additional information. In addition, flowcharts supplied in Appendix D illustrate the general and reiterative procedures described.

COMPUTATION OF ELECTRICAL QUALITIES

The electrical quality of a cell may be defined in a variety of ways. However, the following requirements appear to be desirable characteristics for a definition of quality suitable for accelerated life tests:

(1) Quality must be defined so that the quality of a cell can be quantitatively determined at any time during its operational life. (This precludes, for example, the use of lifetime itself as a definition of quality because the lifetime is not known until the cell fails.)

(2) Quality must be defined so that it ultimately degrades when the cell is operated for long periods of time. (This does not preclude transitional, short-term improvements in cell quality.)

(3) Quality must be defined so that increasing time rates of degradation of quality are obtained when the cell is operated at increasing stress levels. (This requirement precludes inconsistent definitions of increasing levels of stress and quality.)

(4) Quality must be defined so that vendors cannot inflate quality ratings without commensurate benefits to the user.

(5) Quality must be defined in terms of quantitative measurements that can be performed easily and be verified independently in standard laboratories.

(6) Quality must be defined so that it can be related to the user's definition of failure.

When possible, electrical qualities Q_E should be computed in accord with the following expression:

$$\frac{Q_E \geqslant 1}{\Delta E n g'} \, , \tag{65}$$

where n denotes the hourly rate of charge or discharge; ΔE denotes the incremental voltage difference at the cell terminals between the beginning and the end of each charge for voltage qualities under charge, or between the beginning and the end of each discharge for voltage qualities under discharge; g' denotes the specific mass of the cell in grams per ampere-hour capacity of the cell. Both n and g' are based on the manufacturer's rating of ampere-hour capacity. When measured in this way, electrical qualities can be expressed in units of reciprocal ohms (mhos) per gram.

Electrical qualities ordinarily will be defined in terms of the intended-use charge and discharge specifications, which usually means less than 100-percent depth of discharge but may include any amount of overcharge and a wide variety of rates and temperatures specified for each intended-use situation. When actual intended-use conditions are variable, such as for variable eclipse durations or for variable load profiles, the qualities must be defined in terms of the maximum depth of discharge and the minimum duration of charge at an environmental temperature existing with the maximum anticipated discharge rate. When actual intended-use conditions are unknown, the discharge qualities should, for test purposes, be defined as a 50-percent depth of discharge at a 0.5 hourly, or $2C$, rate and charging qualities should be defined in terms of 100 percent recharge at a $1C$ rate. All depths of discharge should be defined in terms of the manufacturer's rated ampere-hour capacity C.

The definition of quality in Equation 65 will permit comparisons of qualities among manufacturers, cell sizes, and cell types. If Equation 65 cannot be used, as for example in a voltage-limited application, any definition of quality that satisfies the above six criteria may be used.

PREDICTION OF PARAMETRIC FAILURES OVER TIME

To assist in the development of valid predictive techniques for each stress level, at least five predictions should be made of the time intervals at which the electrical quality is expected to have degraded to a level associated with a parametric failure, as defined below. Such predictions should be made at five

equally spaced values for the average electrical quality of each matched group of cells and for each individual cell in the group between the start of the test and a quality level that must be previously defined as an operational failure, as described below. The predictions themselves may be classified as occurring either within a stress level for a specified test or between stress levels for a specified test.

Estimation of Time to Operational Failure

A cell is said to be an operational failure whenever the quality of the cell falls to a preset unacceptable level. Let $\overline{Q}_0$ denote the average initial electrical quality for a selected matched group of cells in a selected experiment. Let Q_f denote the preset quality level associated with operational failure, and let $\overline{Q}(t^*)$ denote the average quality for the matched group of cells at time t^*, where t^* denotes a fixed time in the early-life measurements.

An initial estimate of the time rate of degradation of the electrical quality is given by

$$R = \frac{\overline{Q}(t^*) - \overline{Q}_0}{t^* - t_0}$$

$$= \frac{\Delta\overline{Q}(t^*)}{\Delta t} \tag{66}$$

where $\Delta Q(t^*)$ denotes the measured change in quality level that is observed to occur after a time interval Δt has elapsed from the beginning of the experiment. If the degradation of electrical quality occurs over time at a constant rate R, the time required for the quality level to decrease to Q_f is estimated by

$$t_f = \frac{Q_f - \overline{Q}_0}{R} \quad . \tag{67}$$

This estimate of the time to operational failure is based on an assumed linear degradation of electrical quality. (Such linear degradations may not occur in actual accelerated tests, in which case more general formulas than those given here will be required. These general formulas must be tailored to be consistent with the observed behavior of quality obtained in the early portions of each experiment. For simplicity of exposition, however, it is assumed that the linear relation is valid.)

Figure 22 shows a sketch of linear plots for a set of five stress levels involved in one test. To simplify the plot, it is assumed that the average initial quality $\overline{Q}_0$ is the same for each set of matched cells. The upper dashed line shows an extrapolation of the line that represents the average quality of the matched cells operated at the lowest stress level. The remaining dashed lines are associated with similiar extrapolations for the successively increased levels of stress.
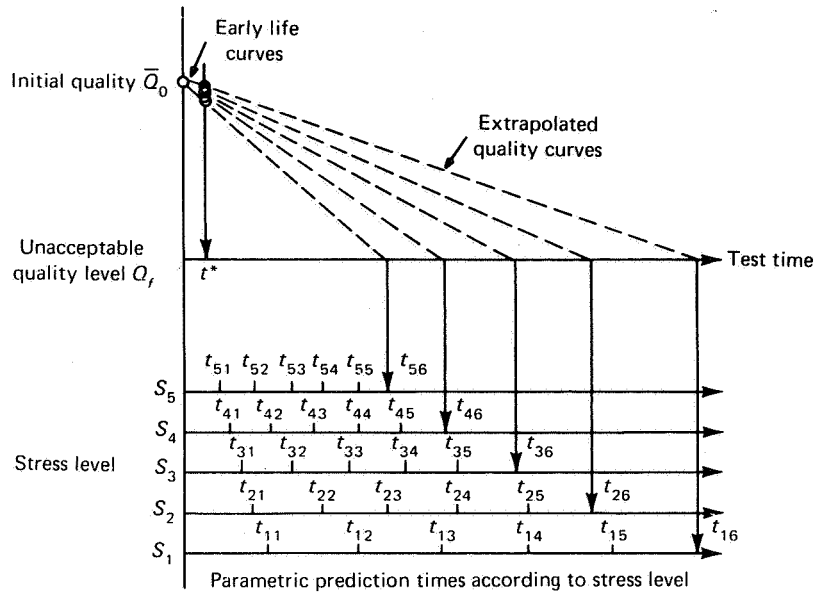
Figure 22—Hypothetical extrapolation of early-life quality curves to determine parametric prediction times.

The intersections of the extrapolated lines with the horizontal line representing Q_f give predictions of the expected time to operational failure. A predicted time is obtained for each stress level. These times are labeled in Figure 22 as $t_{16}, t_{26}, t_{36}, t_{46},$ and t_{56} for the lowest to highest stresses. As suggested by Figure 22, the value of t^* must be less than t_{51}. If possible, a value of $t^* = t_{51}/2$ should be used.

Determination of Parametric Prediction Times

The times at which predictions should be made are obtained by dividing the expected operational life into six equal subintervals. The times associated with the endpoints of these subintervals are called parametric prediction times. A parametric failure, as has been discussed, is said to have occurred whenever the quality of a cell degrades an additional one-sixth of the initial range of acceptable quality, with the exception that the final parametric failure coincides in time with operational failure. With linear degradations of quality, the parametric predition times are the predicted times at which the parametric failures are expected to occur. These parametric prediction times are shown in the horizontal scales at the bottom of the plot in Figure 22. One scale is shown for each of the five stress levels. Thus, for example, at stress level S_4 the parametric prediction times are labeled as $t_{41}, t_{42}, t_{43}, t_{44}, t_{45},$ and the estimated operational failure time is labeled t_{46}. In general, the parametric

prediction times are denoted by t_{ij}, where i denotes the stress level ($i = 1, \ldots,$ 5) and j denotes the index of the parametric prediction time ($j = 1, \ldots, 5$); this gives a total of 25 parametric prediction times for each test program.

Because of the initial uncertainties in the shape of the quality degradation curve over time, the extent of the extrapolation, and so forth, early estimates of expected life at each stress level may be grossly incorrect. If these estimates are incorrect, determinations of the parametric prediction times will also be incorrect. To update and correct these early estimates, whenever a parametric prediction time has arrived, a measurement of the remaining expected life should be made and updated values should be derived for the remaining parametric prediction times. For example, at time t_{11} a new estimate should be made of t_{16}; from this value the four remaining prediction times should be obtained by dividing the new expected remaining time on test ($t_{16} - t_{11}$) by 5 to obtain updated estimates for $t_{12}, t_{13}, t_{14},$ and t_{15}. When the updated time t_{12} has elapsed, another updated estimate of t_{16} should be made, and the three remaining prediction times should be obtained by dividing the new expected remaining time on test ($t_{16} - t_{12}$) by 4 to obtain updated estimates of $t_{13}, t_{14}, t_{15},$ and so on.

As suggested by Figure 22, the initial extrapolation of electrical quality over time at a given stress level yields a predicted average quality for a matched group of cells at any time between t^* and the expected end of the test. Thus, at t^*, the extrapolation procedure automatically generates predictions of the quality levels at all of the parametric prediction times. For example, at stress level S_1, the initial extrapolation beyond time t^* yields a parametric prediction time at t_{11} and a predicted quality level $\hat{Q}(t_{11})$ at that time. When time t_{11} arrives, an updated extrapolation beyond t_{11} will yield an updated parametric prediction time at t_{12} and a predicted quality level $\hat{Q}(t_{12})$. In general, whenever a parametric failure time arrives, the updated extrapolation will yield an updated estimate of the next parametric prediction time and an updated estimate of the quality level at that time. When the penultimate parametric failure time has arrived, the updated extrapolation will yield an updated estimate of the average time at which operational failure is expected to occur for the matched group of cells.

For stress level S_1, six extrapolated lines will be obtained for the average quality level of the matched group of cells. The first line is generated at time t^*, the second at time t_{11}, the third at time t_{12}, and so forth until the last is generated at time t_{15}. Each of these lines yields predictions of quality for all times between the time that the line was first constructed and the predicted time to operational failure. Thus, whenever a parametric prediction time arrives, the observed average quality that exists at that time for a matched group of cells can be compared with the predicted quality obtained from each extrapolation line generated prior to that time. For example, at time t_{13} the observed average quality $\bar{Q}(t_{13})$ may be compared with three earlier predictions of $\hat{Q}(t_{13})$. The first prediction was generated at time t^*, the second

prediction was generated by the extrapolation line constructed at the first parametric prediction time t_{11}, and the third prediction was generated by the extrapolation line constructed at the second parametric prediction time t_{12}.

Table 23 illustrates a tabulation of the predicted and observed quality levels. The main diagonal entries consist of the observed average quality of a matched group of cells at the actual measurement time shown by the entries in the first column. The entries above the main diagonal are predictions obtained from previously constructed extrapolation lines; these predicted qualities may be filled in at the actual time of measurement. The table shows that at t_{11}, only one prediction is obtained of the quality, whereas five predictions are made of the quality at t_{15}.

In analyzing these predicted and observed qualities, comparisons should first be made between the observed and predicted qualities at the end of each parametric prediction interval. In the table, these 1-period comparisons involve comparisons of the adjacent entries in the same columns for the two central diagonals, that is, $\overline{Q}(t_{11})$ with $\hat{Q}(t_{11})$, $\overline{Q}(t_{12})$ with the entry immediately above it, $\overline{Q}(t_{13})$ with the entry immediately above it, and so on. Five such 1-period comparisons are possible. In a similar way, the table shows that four 2-period comparisons are available: $\overline{Q}(t_{12})$ with the entry two rows above it, $\overline{Q}(t_{13})$ with the entry two rows above it, and so on. A single comparison involving a 5-period prediction is available as shown by the last column of the table.

Each of these comparisons should be made for each of the five stress levels for each of the five experiments. Thus, a total of 25 such tables would be generated. Because each table involves 15 predicted quality levels, a total of $25 \times 15 = 375$ predictions of average quality for matched groups of cells would be made in the accelerated test program. By making such predictions and improving the methods for extrapolation during the course of the program, it is

Table 23—*Predicted and observed quality levels for each experiment.*

Actual Measurement Time	Predicted and Observed Qualities[a]				
t^*	$\hat{Q}(t_{11})$	$\hat{Q}(t_{12})$	$\hat{Q}(t_{13})$	$\hat{Q}(t_{14})$	$\hat{Q}(t_{15})$
t_{11}	$\overline{Q}(t_{11})$	$\hat{Q}(t_{12})$	$\hat{Q}(t_{13})$	$\hat{Q}(t_{14})$	$\hat{Q}(t_{15})$
t_{12}		$\overline{Q}(t_{12})$	$\hat{Q}(t_{13})$	$\hat{Q}(t_{14})$	$\hat{Q}(t_{15})$
t_{13}			$\overline{Q}(t_{13})$	$\hat{Q}(t_{14})$	$\hat{Q}(t_{15})$
t_{14}				$\overline{Q}(t_{14})$	$\hat{Q}(t_{15})$
t_{15}					$\overline{Q}(t_{15})$

[a]Predicted quality levels are denoted by a circumflex; observed average qualities are denoted by a bar.

expected that much improved procedures for predicting degradation of quality at a given stress level will be developed during the course of the test program. This would certainly be expected if the degradations were found to be nonlinear over time.

Predictions of Parametric Failures Across Stress Levels

The preceding section was concerned with predictions of quality levels when the cells are operated at a fixed level of stress. To insure the development of valid techniques for predicting qualities at a lower stress level from data obtained at a higher stress level, at least five parametric failure predictions must be made at approximately equal intervals of stress for each pair of adjacent stress levels in any one experiment. For example, data obtained at the highest temperature level should be used to predict times at which parametric failures are expected to occur at the second-highest temperature level; the data obtained at this temperature should be used to predict parametric failures at the next lower temperature; and so on. When these predictive attempts are judged successful, predictions should be made for all possible pairs of stress levels, with particular emphasis on prediction of electrical quality at the stress level associated with the intended-use condition.

This kind of prediction is fundamental to accelerated testing where the aim is to predict quality levels at an intended-use stress level from data obtained at higher-than-normal stress levels.

Again, for convenience of exposition, it is assumed that the degradation of quality occurs linearly over time. Because this is not likely to be observed in practice, more general procedures than those given below should be evolved during an actual life test program.

With linear degradations of quality over time, there are expected to be five rates of degradation associated with the five stress levels in each experiment. These rates are denoted by $R_1, R_2, \ldots, R_5$ and correspond to the normal stress level S_1 through the most severe stress level S_5. The acceleration factor λ_{51} between S_5 and S_1, for example, is given by the ratio of R_5 to R_1,

$$\lambda_{51} = \frac{R_5}{R_1} . \tag{68}$$

In physical terms, this factor is equal to the number of hours of operation at a normal stress level that is required to produce the same decrease in quality that occurs in 1 hr at stress level S_5. More generally,

$$\lambda_{ij} = \frac{R_i}{R_j} \tag{69}$$

is the acceleration factor obtained as the ratio of the degradation rate at stress level i to the degradation rate at stress level j. Under the linearity assumptions, as soon as the degradation rates are known, the acceleration factors can be

computed. A prediction of the quality level at a normal stress level can then be obtained as shown by the following example.

Suppose the average quality of the matched cells at stress level S_5 is observed to be equal to Q' at time t'. It is predicted that the average quality of the matched cells operated at the normal stress level will also equal Q' at a later time equal to $\lambda_{51} t'$. In this way, predictions of the future quality can be made for the normal stress level from the observed qualities at the higher-than-normal stress level and the computed acceleration factors. (The difficulties with this procedure are many; nonlinearities, scatter in the data, and so forth, conspire to prevent the development of a generally acceptable procedure.)

It should be noted that in the above predictions within and across stress levels, the formulations have been expressed in terms of the average quality of a matched group of cells. Whenever possible, it is recommended that predictions be made for individual cells using basically the same methods that are applied to groups of cells. Qualities of individual cells would be used instead of the average quality of a matched group of cells.

Finally, each predicted time to reach a specified degraded level of electrical quality should be compared with the observed actual time. These comparisons should be made within each stress level and between stress levels. The predictions should be judged for statistical validity using, when possible, standard statistical techniques. All changes in predictive methods during the test program should be documented.

Acceleration factors could be computed for those predictions calculated and validated between different stress levels. For the case of linear degradations of quality, the acceleration factors are computed by taking ratios of degradation rates. In more complex situations, different computational procedures are required; a summary of these methods is given in Sections 3 and 4.

10 DESTRUCTIVE TESTING AND TEAR-DOWN ANALYSIS

DESTRUCTIVE TESTING

In an ideal accelerated test for spacecraft batteries, a blend of nondestructive and destructive testing is advantageous. The previous sections have been concerned primarily with nondestructive tests. In this section, some of the characteristics of destructive testing are considered. For an ideal test, it is argued that the degradation processes that lead to failure may be identified before failure occurs by making a destructive examination of cells that are operationally good. If these processes are identified, the physical approach to accelerated testing can associate this information with physical stresses; thus, failure predictions could be made, from which improvements in cell design could eliminate failures or changes in environmental conditions could reduce the operating stresses.

Destructive tests can be included in an accelerated test program in several ways:

(1) A cell may be destroyed by operating the cell at high levels of stress.
(2) A cell may be removed from test and subjected to a destructive examination before failure.
(3) A cell may be examined after failure to determine the immediate cause of failure.
(4) A cell may be examined after failure to affirm that failure mechanisms were unchanged by the accelerated test conditions.

In the first case, the cell is considered to have ceased to function as a cell; it is removed from test, and an autopsy is performed to determine the failure determinants and mechanisms. In the second case, a cell that is operating satisfactorily is removed from test and is destructively examined to infer its operational state at the time it was removed from test. In the third and fourth cases, destructive tests are used as diagnostic tools to aid in the physical interpretation of the results from the accelerated test program.

Destruction of a Cell on Test

Operational failure of a cell on test may result from either intentional or unintentional destruction. If the destruction is intentional, it usually means

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that high stress levels were deliberately chosen in order to determine the life of the cell under especially adverse conditions. In some accelerated tests, the stress levels are increased continuously until failure occurs. Such testing is not considered to be an ideal accelerated test because the cell may have failed for a different reason than that which would occur under normal stress levels. Nevertheless, in preliminary or exploratory experiments, useful information may sometimes be obtained by such deliberate destruction. Destruction is especially useful if the cell is subjected to a critical physical examination designed to indicate what degradation processes caused the failure to occur.

In other instances, a cell may cease to operate during a test even though the stress levels were not intended to exceed those maximum levels of stress consistent with normal failure processes. In these cases, a considerable amount of information may be obtained by a thorough autopsy of the cell. Causes of catastrophic failures might be revealed, and, hence, remedial action could be taken by the manufacturer.

Failure analysis procedures to perform autopsies have been outlined elsewhere for nickel-cadmium and silver-zinc cells (Reference 55). Hence, these will not be discussed in detail here. Work has also been performed on tear-down analyses of unused, nonfailed cells (Reference 56). The purpose of these tests is to provide reference data with which the autopsy data might be compared in an effort to identify the degradation processes. Both of these procedures or analyses are applicable to the parametric failures discussed elsewhere.

Destruction of Operational Cells

As described in Section 9, a sequence of parametric failure modes may be used to monitor the transition of cells through successive parametric failure modes. This may be done at each stress level. The transitions would be expected to occur more rapidly at the higher stress level.

In some instances, it may be desirable to select a cell that had failed in a given parametric mode and to destructively examine the cell. This would be done to gain further understanding of the state of degradation, failure mechanisms, and so forth, that are not detectable or identifiable by means of the nondestructive measurements made during an ideal accelerated test. Consequently, it is recommended that a few operationally good cells be destructively examined during the course of an ideal accelerated test to assess the value of such examinations. Based on the results of such examinations, it may be appropriate to increase or decrease the frequency of such destructive examinations.

In summary, the destructive examination of operational cells after the lapse of various test times is recommended as a method of monitoring the degradation processes during the course of operational life. Because the cell is destroyed by the examination, the usefulness of the information obtained depends to a large extent on the similarities between the destroyed cell and the

other operational cells in the same parametric failure mode at the same stress level. That is, to be most useful, it must be possible to infer that the same state of physical degradation holds for the remaining associated cells. In principle, this may be done by careful selection of the cells to be used at each stress condition. With these restrictions, the physical examinations may then yield information that is useful in establishing the relations between states of physical degradation and thus provide valuable information for an analysis of the type described under ideal physical accelerated tests.

TEAR-DOWN ANALYSIS PROCEDURES

A tear-down analysis should be performed on five randomly selected cells from each group of matched cells before the accelerated life test begins. The remaining cells are then put on test.

At five successive, approximately equally spaced times during the test, an additional randomly selected cell should be removed from each group of cells operating at each test condition. These cells should be subjected to the tear-down procedures; the times should correspond with the times t_{ij} at which the parametric failure predictions are made (see Section 9). The tear-down analyses performed at these times will permit the determination of whether the dominant failure mechanism has changed. Moreover, the tear-down procedures will help to determine whether degradation of electrical qualities can be correlated with degradation of the physical and chemical properties of the cells. This correlation might be achieved through comparison of the results of the tear-down analyses during the tests with the results obtained on the cells before the tests began.

Tear-down analysis places emphasis on cell weights, dimensions, and chemical composition, as opposed to failure analysis, which places emphasis on the electrical characteristics of a cell. Data obtained from the tear-down analysis of uncycled cells provide information for determining specific physical and chemical changes that have occurred in cycled cells after subjection to similar analytical procedures. In this way it is conceptually possible to identify the degradation processes and to associate degradation rates of qualities with the identified processes. Evidence that a change in degradation process has not occurred during an accelerated life test is a prerequisite for the correct analysis of the data for predictive purposes.

(The following tear-down procedure is for nickel-cadmium spacecraft cells; similar procedures for other types of spacecraft cell are not documented, but should follow the example given.)

The tear-down analysis for nickel-cadmium cells is performed on the cells in the discharged condition. Information from the analysis is recorded on an analysis sheet similar to that shown in Figure 23. The numbers of the items (1 through 18) in the procedure will be referred to in the following discussion, which is taken from Reference 66.

Manufacturer and serial no. _____ Rated capacity _____
Analysis no. _____ Cell code no. _____
Date _____ Analyst _____ Location _____

1. Sketch cell on reverse side showing all dimensions
2. Clean, dry weight of cell before cutting case _____
3. Weight of cell after cutting case _____
4. Weights of individual cell components after extraction and drying:
   - (a) Separators _____ (e) Can liner, if present _____
   - (b) Total negatives _____ (f) KOH from analysis _____
   - (c) Total positives _____ (g) K_2CO_3 from analysis _____
   - (d) Cell can and terminals _____ (h) Other, list below _____
   - Total component weight _____
5. Weight H_2O in cell (Item 3 minus total component weight) _____
6. Weights of individual negative electrodes:
   - (1) ___ (5) ___ (9) ___ (13) ___ (17) ___
   - (2) ___ (6) ___ (10) ___ (14) ___ (18) ___
   - (3) ___ (7) ___ (11) ___ (15) ___ (19) ___
   - (4) ___ (8) ___ (12) ___ (16) ___ (20) ___
   - Average weight _____
7. Weights of individual positive electrodes:
   - (1) ___ (5) ___ (9) ___ (13) ___ (17) ___
   - (2) ___ (6) ___ (10) ___ (14) ___ (18) ___
   - (3) ___ (7) ___ (11) ___ (15) ___ (19) ___
   - (4) ___ (8) ___ (12) ___ (16) ___ (20) ___
8. Dimensions of fifth negative and fifth positive (sketch on reverse)
9. Volume (from dimensions) of negative ___ cm^3, of positive ___ cm^3
10. Analysis of negative no. _____ : _____ wt percent active material, _____ wt percent inactive cadmium
11. Analysis of positive no. _____ : _____ wt percent active material
12. Capacity of negative no. _____ : H_2-free _____ A-hr, discharge _____ A-hr
13. Discharge capacity of positive no. _____ : _____ A-hr
14. Terminal-to-terminal resistance _____ Ω
15. Hydrogen-reduction analysis of positive no. ____ : _____ wt percent active material
16. Appearance and condition of separator
17. Separator analysis (optional):
    - Identification by infrared spectrum _____
    - Analysis for cadmium _____
    - Analysis for nickel _____
18. Other observations and notes:

Figure 23—Tear-down analysis data sheet for nickel-cadmium cells.

Cell Description (Items 1 and 2)

Apart from the information needed to complete the top of the data sheet, a sketch of the cell is required. This sketch should include all exterior dimensions of case and terminals and should indicate the extent to which the case is concave or convex by showing measurements near the top and bottom and at the center of each cell face. The total clean dry weight completes the description of the complete cell.

Removal of Cell Case (Item 3)

The cell case is removed by first cutting around the cell top just below the weld. Care should be taken not to damage the separators or terminal fittings (tabs, collectors, and so forth). Once all four sides have been cut, the cell is reweighed to determine the amount of case material lost. The bottom of the

cell is then pulled away from the top. The electrode pack remains attached to the terminal fittings on the top.

Electrolyte Extraction (Items 4f and 4g)

Immediately after removal of the case bottom, any restraining bands on the electrode pack are removed. The pack is then placed in a Soxhlet extractor with about 800 ml of distilled (or deionized) water. The inside of the case bottom is rinsed with distilled water; this rinse water is added to that in the extractor. The extractor is run for 2 days under a nitrogen atmosphere to remove all KOH and K_2CO_3 from the cell components. After cooling the extractor, the water containing the extracted KOH and K_2CO_3 is transferred to a 1-l volumetric flask and diluted to volume. The KOH and K_2CO_3 contents are then determined volumetrically by titrating 50-ml aliquots with $1N$ standard acid using phenolphthalein and methyl orange indicators.

Weights and Dimensions of Components (Items 4a to 4i and to 9)

After extraction, the electrode pack is disassembled by cutting the individual electrode tabs. The separators are removed and the negative and positive electrodes are stacked in separate piles in the same order as they were in the cell. The electrodes and separators are then dried at 333 K (60° C) for 24 hours.

The total weight of the individual electrodes under items 6 and 7 will differ from that recorded in items 4b and 4c by the weight of the tabs, which are carefully removed from each electrode after item 5 is recorded. The dimensions of one positive and one negative electrode are measured (item 8) so that typical volumes can be calculated (item 9).

Chemical Analysis of Electrodes (Items 10 and 11)

The procedures for the chemical analysis of both positive and negative electrodes are taken from Reference 66. For the negative electrode, both cadmium-hydroxide and cadmium-metal content are determined. The $Cd(OH)_2$ is extracted into an NH_4OH/NH_4Cl solution, which does not dissolve metallic cadmium. The metallic cadmium is dissolved in a nitric acid solution, and the cadmium content of both solutions is determined by titration with a standard ethylenediamine tetraacetic acid (EDTA) reagent solution.

For the positive electrode, the nickel hydroxide is extracted into an NH_4OH/NH_4Cl solution as above. Little attack of the sintered nickel plaque occurs under conditions that exclude oxygen. After extraction, the electrode is washed and dried; the weight difference gives the amount of nickel hydroxide.

Negative Electrode Analysis

Both cadmium-hydroxide and metallic-cadmium content are determined in this procedure. The cadmium hydroxide is extracted into an ammonium-hydroxide/ammonium-chloride solution, whereas the metallic cadmium does

not dissolve in this solution. Metallic-cadmium content is determined after the extracted portion of the sample is dissolved in acid. Cadmium content is determined in the two solutions by titration with standard EDTA. The following reagent solutions are required:

(1) Standard cadmium: 1 ml $\cong$ 2.5 mg cadmium: Dissolve 4.0771 g anhydrous cadmium chloride in water and dilute to 1 l.

(2) EDTA solution, 0.05M: Dissolve 18.6 g disodium ethylenediamine tetraacetate in distilled water and dilute to 1 l. For a 0.01M EDTA solution, dilute 100 ml of 0.05M EDTA to 500 ml with distilled water.

(3) Buffer: Dissolve 54 g ammonium chloride in approximately 300 ml distilled water. Add 350 ml ammonium hydroxide and dilute to 1 l with distilled water (pH = 10).

(4) Ten-percent formaldehyde solution: Dilute 28 ml 56-percent formaldehyde to 100 ml with distilled water.

(5) Ten-percent cyanide solution: Dissolve 25 g sodium cyanide in 250 ml distilled water.

(6) Eriochrome Black T: Mix 0.125 g Eriochrome Black T with 50 g sodium chloride.

The EDTA solution is standardized as follows: Transfer 50.00-ml aliquots of the standard cadmium solution to 250-ml beakers. Dilute to approximately 100 ml with distilled water. With ammonium hydroxide, adjust the pH to approximately 10. Before removing the sample from the pH meter, add 10 ml buffer and stir sample. Remove sample and add 5 ml 10-percent sodium cyanide. Place beaker on a magnetic stirrer and add enough Eriochrome Black T to impart a medium-blue color to the sample solution. Add sufficient 10-percent formaldehyde solution until a wine-red color is obtained, and add approximately 1 to 2 ml in excess. Titrate immediately with EDTA solution until a permanent blue color is obtained. Calculate EDTA factor, milligrams of cadmium per milliliter of EDTA.

The electrode sample is treated as follows: Heat approximately 400 ml distilled water and 20 g of NH_4Cl in a 600-ml beaker to 343 to 353 K (70° to 80° C). During this heating and throughout the procedure, nitrogen gas must be bubbled through to provide an oxygen-free solution to prevent oxidation of metallic cadmium. (A watch glass placed over the beaker prevents spattering of the solution.) When the temperature of the solution reaches 343 to 353 K (70° to 80° C), add 100 ml of concentrated NH_4OH and the accurately weighed electrode sample (3.0 to 3.5 g). Continue heating at 343 to 353 K (70° to 80° C) for 2 hr with occasional stirring. After 1 hr, add an additional 50 ml of NH_4OH to replace that lost by evaporation. The solutions must never lose all their NH_4OH or the metallic cadmium will be attacked. After the extraction is complete, the remainder of the electrode is washed with distilled water, and this washing is added to the NH_4OH/NH_4Cl solution. The solution is transferred to a 100-ml volumetric flask and diluted to volume.

The remainder of the electrode sample containing metallic cadmium is dissolved in 5 to 10 ml of 1:1 nitric acid. Evaporate the solution to a syrupy consistency, dilute with 10 ml of distilled water, and evaporate again to remove excess acid from the solution. Transfer the solution to a 500-ml volumetric flask and dilute to volume.

Analysis of the two solutions is performed in the same manner as the standardization of the EDTA solution except that 10 ml instead of 5 ml of 10 percent sodium cyanide is added to the aliquots containing the dissolved electrode to complex the dissolved nickel. If the electrode substrate contains iron, such as when the electrode plaque is formed on nickel-plated steel, a precipitate of iron hydroxide is formed when the pH of the solution is adjusted to 10. This precipitate must be removed by filtration before the remainder of the procedure can be performed. The various chemical reactions and complex formations due to the addition of cyanide and formaldehyde are discussed by Welcher (Reference 67).

The weight percent of $Cd(OH)_2$ in the electrode sample (item 10) is calculated by

percent $Cd(OH)_2$ =

$$\frac{(ml\ EDTA)\ (mg\ Cd/ml\ EDTA)\ (1000/50)[Cd(OH)_2/Cd]\ 100}{(wt\ sample)\ (1000\ mg/g)} . \quad (70)$$

The weight percent metallic cadmium (item 10) is calculated by

$$percent\ Cd = \frac{(ml\ EDTA)\ (mg\ Cd/ml\ EDTA)\ (500/50)\ 100}{(wt\ sample)\ (1000\ mg/g)} . \quad (71)$$

It must be noted that the factors "ml EDTA" in Equations 70 and 71 are different and refer, respectively, to the volume of titrate required to titrate the solution containing extracted $Cd(OH)_2$ and the volume required to titrate the solution containing the dissolved electrode sample.

Positive Electrode Analysis

Nickel hydroxide, the active material in the positive electrode, is extracted into a solution of ammonium-hydroxide/ammonium-chloride. The attack on sintered nickel is small under conditions that exclude oxygen. The following procedure is used:

Place approximately 250 ml of distilled water and 20 g of NH_4Cl in a 400-ml beaker and heat to 343 to 353 K ($70°$ to $80°$ C). Nitrogen is bubbled through the solution, as in the analysis of negative electrodes. When the temperature reaches 343 to 353 K ($70°$ to $80°$ C), add 75 ml of concentrated NH_4OH to the solution, and place the accurately weighed positive electrode sample (about 3.5 g) in the solution. Continue heating the solution at 343 to 353 K ($70°$ to $80°$ C) for 3 to 4 hr with occasional stirring. Add 25 ml of NH_4OH each hour. This procedure is repeated with fresh solutions until no blue coloration appears

in the solution after 1 hr. When no more nickel can be extracted from the electrode sample, wash the sample with distilled water, and dry overnight at $333°$ K ($60°$ C). The weight percent of active material (item 11) is calculated by

percent active material =

$$\frac{[(wt\ sample\ before\ extraction) - (wt\ sample\ after\ extraction)]\ 100}{wt\ sample\ before\ extraction} . \quad (72)$$

Extraction of nickel hydroxide in this manner also extracts cobalt hydroxide. If cobalt content is to be determined, the separate extract solutions are combined for cobalt analysis; otherwise they are discarded.

Electrical Performance of Negative Electrodes (Item 12)

A selected negative electrode is charged at about $C/3$-rate calculated from the manufacturer's rated capacity and the number of electrodes in the cell. A planar nickel counter electrode is used, and the potential of the test electrode is monitored against an Hg/HgO reference electrode, as shown in Figure 24. Charging is continued beyond the hydrogen-free capacity of the electrode, which is when the first bubble of hydrogen appears or when the break occurs in the voltage-time curve obtained, as shown at point A in Figure 25. The discharge capacity to the knee of the discharge curve, as shown at point A in Figure 25, is determined at the calculated $C/2$-rate.

T	test electrode
C	sheet-nickel counter electrodes, one on each side of test electrode
R	Hg/HgO reference electrode
A	ammeter
Rec	recording potentiometer
PS	constant-current power supply
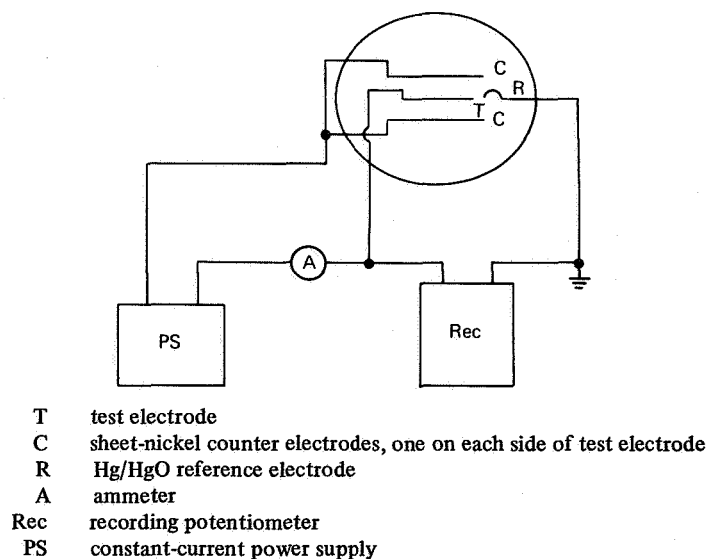
Figure 24—Electrical circuit for obtaining single-electrode capacities.

Figure 25—Charging curve for single negative electrode from a 20-A-hr nickel-cadmium cell (Reference 66). Point A is the extrapolated knee used to determine the hydrogen-free capacity. The current was 0.5 A.

Electrochemical Performances of Positive Electrodes (Item 13)

The same procedure is used as for the negative electrode except that near the end of charge an inflection in the voltage-time curve is not obtained. Charge at the calculated $C/3$-rate is, therefore, carried out for a total of 4 hr before the $C/2$-discharge. The discharge capacity is again calculated to the knee of the discharge curve (Figure 26).
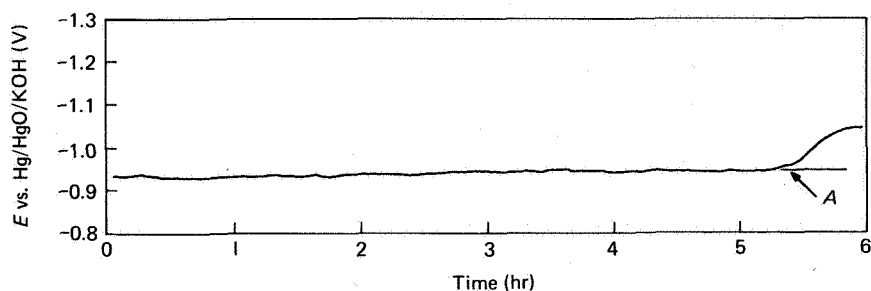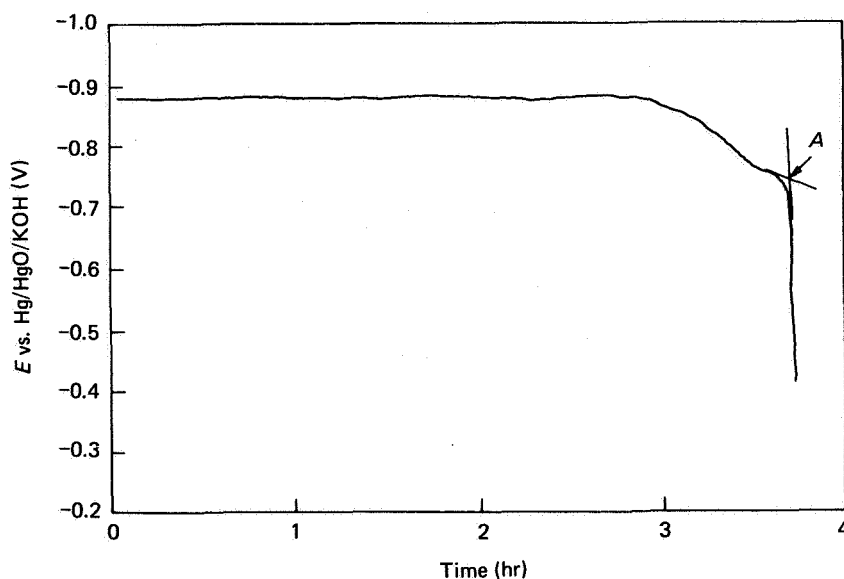

Figure 26—Discharge curve for single negative electrode from a 20-A-hr nickel-cadmium cell (Reference 66). Point A is the extrapolated knee used to determine the discharge capacity. The current was 0.75 A.

Terminal-to-Terminal Resistance (Item 14)

The terminal-to-terminal resistance is measured on the cell top after the tabs have been cut and the electrodes removed; an ordinary ohmmeter is used. If there is no electrical leakage across the terminal insulation, the resistance should be infinite.

Hydrogen Reduction Analysis (Item 15)

This step is reflected on the data sheet as a check on item 11, but it need not be done in connection with the accelerated life test program.

Appearance and Condition of Separator (Items 16 and 17)

Item 16 refers to a visual inspection of the separators for pinholes, burning, penetration, discoloration, and so forth. Item 17 is an optional procedure if further characterization is believed necessary. For example, if it is believed that a separator lot number has been changed for a series of cells, identification of the separator material and oxidizable material in it may be helpful.

Other Observations and Analyses (Item 18)

The above procedures describe all of the analyses believed necessary for uncycled cells. For cycled cells that are removed at different times during the test, some of the following analyses may be desirable for providing additional useful information:

(1) Total organic matter in the electrolyte should be determined by a permanganate titration. The total organic matter should include all species from any wetting agents used and from separator breakdown.

(2) Since some manufacturers put LiOH in the electrolyte, the electrolyte should be analyzed for lithium.

(3) Instead of including any cobalt in the active nickel hydroxide analysis, positive electrodes should be analyzed for cobalt.

11 IDENTIFICATION OF FAILURE DETERMINANTS

For an accelerated life test to be valid, the dominant failure mechanism must not change over the range of stress levels used in the test. Associated with the failure mechanism is a failure determinant that uniquely controls the failure mode. Therefore, after each operational cell failure, a failure analysis should be performed to identify the failure determinant and provide the basis for judgment about whether the mechanism changed.

These procedures provide a series of observations and empirical tests that can be performed to indicate subsequently the most probable cause of cell failure. The procedures differ from the tear-down analysis described in Section 10 in that the emphasis is on identifying the failure determinant of a failed cell.

Detailed procedures for nickel-cadmium cells and silver-zinc cells have been described (Reference 66). These failure analysis procedures consist of three parts:

(1) Physical examination of the cell
(2) Characterization of electrical performance
(3) Disassembly of the cell for inspection

These three parts will be briefly discussed.

FAILURE ANALYSIS PROCEDURE FOR NICKEL-CADMIUM CELLS

An outline of the failure analysis procedure for nickel-cadmium cells is given in Table 24, and a typical analysis sheet is shown in Figure 27. Full details of the procedure are given in References 66 and 68. The following comments are intended to explain the entries in the tables.

Physical Examination

Steps 1.1 through 1.9 identify the cell[1] and, as far as possible, list the cell history of use prior to failure. This information is not necessary to arrive at the

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[1] In any failure analysis procedure, a permanent identification mark should be made on the cells (preferably on the cell tops) because the procedures call for washing of the cells and for cell disassembly.

Table 24—*Failure analysis procedure for nickel-cadmium cells.*

1.0 Physical examination. Assign sequential number for battery failure analysis (BFA); this BFA number is entered on the failure analysis data sheet.[a]

   1.1 Record serial or part number and manufacturer of battery or cells. If not marked, inscribe a permanent marking in a convenient location on top of each cell.

   1.2 Record manufacturer's nominal ampere-hour capacity, if known.

   1.3 Record any known ampere-hour capacity measurements obtained by user and their date for each cell.

   1.4 Record person or facility using cell or battery.

   1.5 Record original application of failed battery or cell, including environment and temperature.

   1.6 Record user's current, voltage, and time requirements.

   1.7 Note condensed performance history, including observations on internal pressure and temperature, date of failure, and failure mode.

   1.8 Note any mishaps in use, such as dropping or reverse charging.

   1.9 Detail any irregularities in appearance such as crusty terminals, cracked insulators, or dents. Low-power magnification (5X to 20X) is suggested for inspection of irregularities.

   1.10 Remove cells from a battery connection or from restraining plates; scrub each cell with brush and water, rinse with deionized water, and allow to dry completely before weighing. The cell should be kept free of fingerprints or other source of alkaline contamination. Record weight to the nearest 0.1 g.

   1.11 Perform leak check with 1/4-percent phenolphthalein solution after discharge (Step 2.4). Describe location and extent of any leaks.

   1.12 Record other observations or remarks.

2.0 Electrical performance of individual cells.

   2.1 After adding and adjusting restrainer plate bolts to 0.68 ± 0.06 N-m (6 ± 0.5 lb-in.) torque, record open-circuit voltage. If less than 1.0 V, proceed to Step 2.3; if greater than 1.0 V, proceed to Step 2.2.

   2.2 Discharge at $C/2$-rate to 1.0 V using the first possible of following:

      (a) Capacity from user's earliest data (1.3).

      (b) Manufacturer's nominal capacity (1.2).

      (c) Capacity calculated by dividing weight by 40 g/A-hr (1.10).

   2.3 Charge at $C/3$-rate using the same capacity as determined in Step 2.2. Continue charging for a total of 4 hr. Record voltage-time plot during charging. If voltage exceeds 1.5 V, record time and reduce rate to $C/40$ for the balance of the 4 hr. If voltage fails to exceed 1.2 V in 15 min, remove cell and proceed to Step 2.6.

   2.4 Discharge at $C/2$-rate using the capacity selected in Step 2.2. Stop at 1.0 V.

   2.5 Determine internal impedance using pulse technique.[b] If greater than 0.1 Ω, proceed to Step 3.0.

   2.6 Check for internal shorts by the following sequence:

      (a) Discharge through 1-Ω resistor until cool.

      (b) Short terminals for 16 hr.

      (c) Charge for 5.0 min at $C/10$-rate.

      (d) Read open-circuit voltage immediately and after 24-hr stand. Use high impedance meter (100 000 Ω/V or greater). A decay of more than 0.10 V indicates possible short.

   2.7 If a cell has a discharge time between 1 and 2 hr in Step 2.4, repeat Steps 2.3 and 2.4 until discharge times in Step 2.4 agree within 5 percent. If discharge

Table 24—*Concluded*

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times agree at less than 2 hr, the cells may have been overrated. If discharge times increase with each capacity measurement, the cell may have been influenced by memory or temporarily inactive forms of the electrochemical materials.

3.0 Disassembly instructions.

    3.1 Remove cell can by cutting four sides just below top to avoid damage to separators. Note if electrode pack is wet with electrolyte. Also note any unusual discolorations and their location.

    3.2 Place the electrode pack in a Soxhlet extractor and extract the electrolyte for 48 hr under nitrogen atmosphere. Analyze the extracted electrolyte for KOH and K_2CO_3 by titrating with standard $1.0N$ acid.

    3.3 After removing the electrode pack from the extractor, dry the pack at 333 K (60° C) for 24 hr. Weigh the dry pack. The difference between the cell weight in Step 1.6 and the sum of the dry pack weight plus the weights of KOH and K_2CO_3 from Step 3.2 is the weight of water in the cell.

    3.4 Place the electrode pack between Lucite retaining plates clamped to hold the cell tightly compressed. Place the electrode pack in a beaker with sufficient 30-percent (by weight) KOH to cover electrodes and separators. Allow the complete pack to soak up electrolyte for at least 24 hr. Charge cell in flooded state at $C/3$-rate as determined in Step 2.3 for a time equal to 1.5 times the last discharge time of Step 2.7.

    3.5 Discharge at $C/2$-rate in flooded state. Record potentials of positives and negatives against Hg/HgO reference electrode as functions of time during discharge. Continue discharge until both sets of electrodes have been fully discharged. Determine the cell capacity to point where the sum of half-cell potentials is 1.0 V. Compare this capacity to that obtained in Step 2.4 or 2.7.

    3.6 Disassemble the electrode pack and note any irregularities such as burned or discolored separator and damaged electrodes.

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[a]See Figure 27.   [b]Reference 69.

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failure determinant but may allow subsequent interpretation of failure analysis data to be made more quickly or accurately.

Steps 1.2 and 1.3 are used to determine the cell's ampere-hour capacity C, which is needed (in Parts 2 and 3 of the procedure) to secure electrochemical/ electrical performance data for subsequent diagnosis. The correct capacity may be difficult to obtain for the following reasons: First, capacity measurements require complete charging and discharging of the cell, which may alter active materials in such a way as to alter the failure determinant or make diagnosis more difficult. Second, if previous capacity data are not available, an estimate is needed; such an estimate may be made by dividing the cell weight by 40 g/A-hr (Reference 66).

Steps 1.4 through 1.8 are for information to be obtained from the cell user. If this information is not available, the procedure will still yield a failure determinant. In Step 1.5, the application is given along with a circuit diagram (if pertinent) and any pressure or temperature limitations or other unusual

BFA no. _____

Date started _____

Date concluded _____

1.0 Physical Examination

     1.1   Serial no. _____ Part no. _____ Manufacturer _____

     1.2   Manufacturer's capacity C _____ A-hr

     1.3   User's capacity C:

           Earliest _____ End voltage _____ Current _____ Date _____

           Latest _____ End voltage _____ Current _____ Date _____

     1.4   User _____

     1.5   User's application _____

           Environment _____

           Temperature _____

     1.6   Electrical requirements _____

     1.7   User's observations _____

           Date of failure _____ Failure mode _____

     1.8   Service mishaps _____

     1.9   Irregularities in appearance _____

     1.10 Clean dry weight ____ g; Estimated capacity (weight/40) _____ A-hr

     1.11 Leak check (after Step 2.4) _____ Leak location _____

     1.12 Other observations _____

2.0 Electrical Performance

     2.1   Open-circuit voltage _____

     2.2 $C/2$ discharge time to 1.0 V ____ hr; Based on 1.3 _____ hr,

           1.2 _____ hr, or 1.10 _____ hr.

     2.3 $C/3$ charging _____ A

     2.4 $C/2$ discharge to 1.0 V; t_0 = _____ hr

     2.5   Internal impedance _____ Ω

     2.6   Discharged (a) ____ Shorted (b) ____ Charge ($C/10$, 5 min) (c) _____

           Open circuit voltage: after 5 min _____ , 24 hr _____

     2.7 $C/2$ discharges to 1.0 V; t_1 = ____ hr, t_2 = _____ hr, t_3 = ____ hr

3.0 Disassembly

     3.1   Electrodes wet _____ Discolorations inside _____

     3.2   Electrolyte analysis:

           Volume to which extracted electrolyte was diluted _____ ml

           Sample volume titrated _____ ml

           Normality of acid _____

           Acid to pH 8 _____ ml; Acid to pH 4 _____ ml

           Total KOH _____ g; Total K_2CO_3 _____ g

     3.3   Dry pack weight _____ g; Weight of H_2O in cell _____ g

     3.4 $C/3$ charge _____ A for _____ hr; Based on 2.4 _____ A

           or 2.7 _____ A

     3.5 $C/2$ discharge to total 1.0 V _____ A-hr

           Limiting set of electrodes _____

           Capacity of other set _____ A-hr

     3.6   Appearance of disassembled parts _____

Figure 27—Failure analysis data sheet for nickel-cadmium cells.

environmental conditions (such as vibration, extended storage times before or between uses, and temperature extremes). Step 1.7 is to record the user's interpretation of definition of failure.

Step 1.9 calls for a thorough visual examination of the cell in order to detect any obvious irregularities.

Step 1.10 is self-explanatory, as are Steps 1.11 and 1.12.

Electrical Examination

These tests are used to determine the amount of residual capacity and the extent of any internal resistance changes. The listed steps will detect a temporary memory effect only by its elimination (Reference 66).

The cell open-circuit voltage is the first indicator obtained of electrical performance (Step 2.1). Any voltmeter with a resistance of 1000 Ω/V or more may be used. During Step 2.1, the cell must be carefully bolted between 0.64-cm-thick (1/4-in.-thick) aluminum or steel restraining plates to counteract any distortion of the case. Step 2.2 is to enable the cells to be brought to the same charge level before a capacity check is made in Step 2.4.

In Step 2.3, a charging rate of $C/3$ is recommended to minimize overall failure analysis time. A regulated current supply with voltage limit control should be used for cell charging. If in Step 2.3 the cell voltage fails to rise above 1.2 V in 15 min, the cell may be internally shorted, and Steps 2.3 and 2.4 may be bypassed.

After the cells have been charged for 4 hr, they are discharged at the $C/2$-rate in the constant-current mode. If the discharge step (2.4) must be delayed, the cell should remain on trickle charge at the $C/40$-rate.

The first capacity determination is made by recording the time to reach a discharge voltage of 1.00 ± 0.02 V. A cell with exactly 100-percent capacity should reach this point in 2.0 hr. If the discharge time exceeds 2.0 hr, the initial capacity estimate was too low, and a new capacity value may be calculated and used as in Step 2.7. Comparison of the discharge time with 2 hr will give the correction. A cell with a discharge time of 1 to 2 hr (50- to 100-percent efficiency) should be tentatively classified as a failure. Such specimens should be rechecked later for a reproducible capacity (Step 2.7). A cell with a discharge time under 1 hr should be considered a failed cell.

The internal resistance of all cells should be checked. Step 2.5 uses the pulse technique with an oscilloscope readout to determine the resistance (References 18 and 69). If this technique shows a resistance under 0.1 Ω, the cell may still be either good or internally shorted. Step 2.6 is used to detect the effect of internal shorts. For these particular voltage measurements, a low-drain meter must be used; its impedance should be 100 000 Ω/V or greater. Here, additional experience is needed to judge appropriate limits for the acceptable voltage decay in the 24-hr interval. New cells appear to lose less than 70 mV, with a final voltage value at or above 1.15 V. An arbitrary limit of 100 mV has been selected as an indication of internal shorts.

A cell of doubtful capacity (discharge time of 1 to 2 hr) should be rerun through Steps 2.3 and 2.4. The charge/discharge repetition should continue for up to four cycles or until consecutive discharge times agree within 5 min at a $C/2$-discharge rate. If the discharge time exceeds 2 hr, the cell may have been underrated.

Disassembly

Cell disassembly will confirm any deductions that might have been made during the physical and electrical examinations. The electrolyte analysis (Step 3.2) and weights (Step 3.3) will show changes in the electrolyte. Steps 3.4 and 3.5 will show which set of electrodes limits the available capacity and by how much. Figure 28 gives the circuit diagram for these capacity measurements. Finally, Step 3.6 provides for a description of the individual electrodes, separators, tabs, and other internal components. Since a tear-down analysis has been performed on an uncycled cell, a comparison may be made with the observations in Step 3.6 to identify any irregularities, evidence of degradation, and so on.

In Step 3.1 the can is prepared for electrode removal by being cut around all four sides about 1 cm below the top. The total weight is recorded after cutting. After the electrode pack is withdrawn from the can, it should be noted whether it is damp or dry and whether any random discolorations are visible on the pack or inside the can.

In Step 3.2 the electrode pack is placed in a Soxhlet extractor; inert blocks are used to fill up any free space. A total of about 800 ml of deionized water is added; some of this water is used to rinse the cell can and liner. Nitrogen flow

PS   power supply
RE   Hg/HgO reference electrode
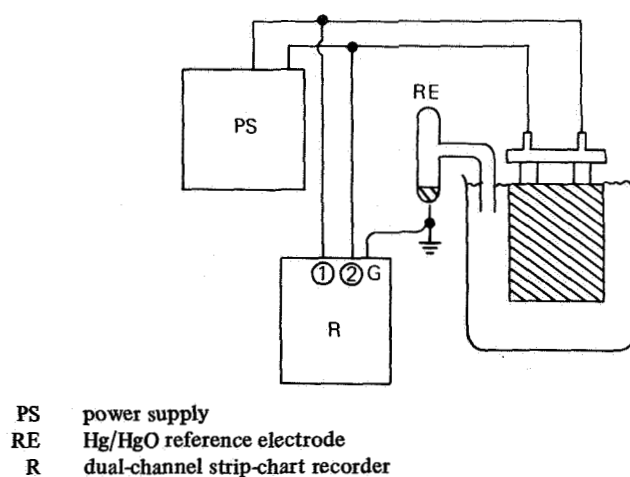R   dual-channel strip-chart recorder

Figure 28—Apparatus for measuring half-cell potentials of both electrodes during flooded-cell operation.

is adjusted to about one bubble per second, and the flow is maintained during the 48-hr boiling period and during cooling afterwards. The extract is transferred to a 1-l volumetric flask, along with the rinse water from boiler and pack holder, and then made up to the mark. Three 50-ml aliquots all placed in 250- or 300-ml Erlenmeyer flasks; two drops of phenolphthalein indicator are added to each and they are titrated with $1N$ standard acid to the endpoint (pink → colorless). The volumes of standard acid used are recorded. Three drops of methyl orange indicator are added to the same solutions and they are titrated to the endpoint (yellow → red orange); these volumes are also recorded.

In Step 3.3 the electrode pack is dried for 24 hr at 333 K (60° C), and the dry weight is recorded. The weight of water is calculated from the difference between the sum of the dry cell components (including KOH and K_2CO_3 from Step 3.2) and the total cell weight.

In Step 3.4 the dried electrode pack is prepared for operation in the flooded, compressed state by using stainless steel screws and nuts to compress the pack between Lucite plates. It is soaked in 30-percent KOH electrolyte in a covered beaker for at least 24 hr. The cell is charged at the $C/3$-rate (as in Step 2.3) for a time equal to 1.5 times the last discharge time of Step 2.7. With an Hg/HgO reference electrode and a dual-channel recorder (as shown in Figure 28), the half-cell potentials of both sets of electrodes are recorded as a function of time.

In Step 3.5 the pack is discharged at a $C/2$-rate until both electrodes reverse polarity, and the time for combined half-cell potentials to fall to 1.0 V is determined. The capacity to this point is calculated and recorded. The electrode that produced the first knee in the voltage-time curves is determined and the total capacity of the nonlimiting electrode is calculated from the time taken to reach the knee on its curve.

In Step 3.6 the electrolyte is washed from the cell under tap water and dried at 333 K (60° C). The separator is unfolded, and the electrodes and separator are examined for damage and defects.

FAILURE ANALYSIS PROCEDURE FOR SILVER-ZINC CELLS

An outline of the failure analysis procedure for silver-zinc cells is given in Table 25, and a typical analysis sheet is given in Figure 29. Full details of the procedure are taken from Reference 66; the following comments are intended to explain the entries in the tables.

Physical Examination

As explained for nickel-cadmium cells, Steps 1.1 through 1.5, 1.7, and 1.9 identify the cell and are used to list (as far as possible) the use history of the cell prior to failure. The capacities listed under Step 1.7 are used in the second part of the procedure to determine charge and discharge rates. In Step 1.6, the cell is washed, dried, and weighed to the nearest 0.1 g. In Step 1.8, a check is made for leaks after the cell has been charged (Step 2.3); leaks that are

Table 25—*Failure analysis procedure for silver-zinc cells.*

1.0   Physical examination: Assign sequential number for battery failure analysis (BFA); this BFA number is entered on the failure analysis data sheet.[a]

    1.1   Record serial or part number of battery or cell. If not permanently marked, inscribe a permanent marking in a convenient location on top of each cell.

    1.2   Record sources of failed battery on cell.

    1.3   Note condensed performance history and date of failure as well as mode of failure if indicated in history.

    1.4   Note any mishap in use, such as dropping or reverse charging.

    1.5   Detail any irregularities in appearance such as crusty terminals, cracked insulation, or bulging. Low-power magnification (5X to 20X) is suggested for inspection of irregularities.

    1.6   Scrub each cell with brush and water, rinse with deionized water, and allow to dry before weighing. A cell should be kept free from fingerprints or other source of alkaline contamination. Record weight to nearest 0.1 g.

    1.7   Record nominal ampere-hour capacity, if known. Also record any known ampere-hour capacity determinations and their date for each cell. Include cutoff voltage, if known.

    1.8   Check for leaks using 1/4-percent phenolphthalein solution after charging (Step 2.3). Describe location and extent of any leaks.

    1.9   Enter other observations such as pressure history or other remarks deemed pertinent to analysis.

2.0   Electrical performance of individual cells

    2.1   Record open-circuit voltage after renewing restrainer plates and providing protective splash enclosure and explosion shield described under the discussions in text. If voltage is less than 1.60 V, proceed to Step 2.3; if more than 1.60 V, proceed to Step 2.2.

    2.2   Discharge at the $C/3$-rate to a cutoff voltage of 1.20 V. Select the value of C in ampere-hours from the first known value of one of the following:

        (*a*)   Capacity most recently measured before failure.

        (*b*)   Nominal capacity specified by manufacturer.

        (*c*)   Capacity calculated by dividing clean cell weight by 25 g/A-hr.

    2.3   Charge with constant current at the $C/3$-rate using the value of C selected in Step 2.2. Continue charging for a total of 4 hr using 1.97 V as an upper voltage limit. Record time to 1.97 V; if necessary, lower current to $C/20$. Continue charge of constant $C/20$-rate to complete the 4-hr total charge time. Record final charge voltage.

    2.4   Discharge at constant current at the $C/2$-rate using 1.20 V as a cutoff. Record time to 1.2 V.

    2.5   Determine internal resistance using the pulse-interrupter device. If resistance is less than 0.020 Ω, internal shorting may be present; proceed to Step 2.6. If resistance is greater than 0.020 Ω, shorting is not likely; proceed to Step 2.7. A high resistance of 0.050 to 0.10 Ω or greater is an indication of unwanted ohmic contributions such as drying out of separators and increased contact resistance at tabs, perhaps caused by corrosion.

    2.6   Check for internal shorts; first conduct repeated discharges at the $C/10$ rate until time to 1.0 V is less than 5 s. Recharge to 0.50 percent of capacity at the $C/10$ rate (this amounts to a 3-min charge at 2 A for a nominal 20-A-hr cell). Measure the recoverable capacity after 1-hr stands using 1.2-V cutoff. A loss of charge in excess of 15 s indicates possible shorting.

Table 25—*Concluded*

2.7	Make judgments based on discharge Step 2.4, internal resistance Step 2.5, and internal short Step 2.6.	
	(*a*)	Cells with discharge times in excess of 2 hr in Step 2.4 which also passed Step 2.5 on internal resistance and Step 2.6 on internal short steps may be regarded as nonfailures.
	(*b*)	Cells with discharge times in Step 2.4 of less than 1 hr regardless of results in Steps 2.5 and 2.6 should be further processed under Step 2.9 below.
	(*c*)	Cells with discharge times in Step 2.4 of between 1 and 2 hr should also be further examined under Step 2.9 below, provided the cells failed either the internal short or the internal resistance tests. If no unusual internal-short or resistance results are found, proceed to Step 2.8.
2.8	Operate cell after inserting a reference electrode of sheet zinc in the free space and partially immersed in free electrolyte. Add 45-percent KOH, saturated with ZnO if necessary. Repeat Steps 2.3 and 2.4 while monitoring potentials between reference electrode to positive and negative cell terminals. Record the elapsed time when the sum of the voltages falls to 1.20 V. Continue operation for 15 min or until the sum of the voltages falls below 1.0 V. If the final discharge time exceeds 1½ hr, Step 3 is probably unnecessary.	
2.9	Recharge (Step 2.3) before disassembly, unless shorts are present.	
3.0 Disassembly instructions		
3.1	Remove cell case, preferably at the seam line.	
3.2	Rapidly unwrap all electrodes and note the following:	
	(*a*)	Penetration of separators.
	(*b*)	Form of loose zinc deposits (treeing or sloughing).
	(*c*)	Estimate proportion of negative material remaining.
	(*d*)	Condition of positive electrodes.
	(*e*)	Preserve questionable components in sealed plastic bag with inert gas (nitrogen, helium, or argon).
3.3	Study questionable structures by metallographic or other analytical tools.	

[a]See Figure 29.   [b]References 18 and 69.

apparent only on cycling may thus be observed. Finally, in Step 1.9, any data that might be of subsequent use in deducing the failure determinant or mechanism should be recorded.

Electrical Examination

Before the electrical tests are performed, the cell must be restrained with suitable restraining plates and placed in a protective splash enclosure with an explosion shield.

If the cell's open-circuit voltage is less than 1.60 V, the cell is charged (Step 2.3). If the open-circuit voltage is greater than 1.60 V, the cell is discharged (Step 2.2) at a $C/3$-rate to a cutoff of 1.20 V before being charged (Step 2.3). Care should be taken during the charging because plastic-cased cells have been

Test station _____ Examiner _____
Date started _____ Ended _____ BFA no. _____
Disposition of cell components _____

1.0   Physical Examination
      1.1   Serial no. _____ Part no. _____
      1.2   Source _____
      1.3   Performance history: Date of failure _____
            Mode of failure _____
      1.4   Service mishaps _____
      1.5   Irregularities in appearance _____
            _____
      1.6   Clean dry weight _____ g _____
      1.7   Capacity: (a)   Measured or reported _____ A-hr
                              End voltage _____ V   Date _____
                        (b)   Manufacturer's rating _____ A-hr
                        (c)   Calculated from 1 A-hr/25 g ____ A-hr
      1.8   Leak check (after 2.3) _____ Location _____
      1.9   Other observations _____

2.0   Electrical Performance
      2.1   Open circuit voltage ____ V
      2.2   Discharge time to 1.20 V _____ hr
      2.3   Capacity selected ____ A-hr; Charging current at $C/3$ A _____
            Charging time to 1.97 V at $C/3$ ___ hr, at $C/20$ ___ hr
      2.4   Discharge time to 1.20 V at $C/2$ _____ hr
      2.5   Internal resistance _____ mΩ
      2.6   Recovered capacity at $C/10$ _____ A-s
      2.7   Classification of cell according to discharge time
            _____ t_1 (<1 hr) ____ , t_2 (1-2 hr) _____ , t_3 (>2 hr)
      2.8   Ampere-hours of electrodes:
            Positive electrodes: (1) _____ (2) _____ (3) ____
            Negative electrodes: (1) _____ (2) _____ (3) ____
      2.9   Charging time to 1.97 V at $C/3$ _____ hr

3.0   Disassembly and Inspection
      3.1   Date of case removal or fracture _____
      3.2   Observations:
            (1)   Penetrated separators: Layers penetrated _____
                                          Layers not penetrated _____
            (2)   Zinc deposits: Treeing _____ Location _____

                                  Sloughing _____ Location _____

            (3)   Condition of zinc electrodes _____ Color _____
            (4)   Proportion of intact zinc _____
            (5)   Condition of positive electrodes _____
            (6)   Other observations _____
      3.3   Metallographic examination of questionable materials _____
            _____
            _____
      3.4   Chemical or physical analysis of questionable materials _____
            _____
            _____

4.0   Notes _____
            _____

Figure 29–Failure analysis data sheet for silver-zinc cells.

known to explode, hence, the precautions of having restraining plates, explosion-proof testing areas, and so on (Reference 66) must be taken.

Charging is performed at a $C/3$-rate until a voltage of 1.97 V is reached. On reaching this voltage the time elapsed is noted, and the charging current reduced to $C/20$ for the remainder of the 4-hr charging period (Step 2.3).

The cells are discharged at a $C/2$-rate to 1.20 V (Step 2.4) to determine the capacity before the internal resistance is measured (References 18 and 69) (Step 2.5). If the measured resistance is less than 0.020 Ω, Step 2.6 for internal shorts is next performed; however, if the resistance is greater than 0.020 Ω, Step 2.6 is omitted. An alternate method of detecting shorts is to charge at a $C/2$-rate until the voltage reaches 1.97 V and then read the open-circuit voltage after a 24-hr stand. If the open-circuit voltage is below 1.86 V, the stand is continued for 10 days; if it is below 1.6 V after either period, shorts are likely.

The information gained from Steps 2.4 through 2.6 is used to classify the cells into nonfailures and possible failures (Step 2.7). To be classified a nonfailure, a working cell must deliver 50 percent or more of its rated capacity at a $C/2$-rate and at a voltage greater than 1.20 V (Reference 66). Any cell with questionable performance or with a capacity below the 50-percent criterion is classed as a possible failure. Such a cell is carried through disassembly without being tested as described in Step 2.8. Only cells having a borderline capacity value and no questionable results for the shorts and resistance tests in Steps 2.5 and 2.6 will be carried through to Step 2.8, which is performed to identify the capacity-limiting electrode.

Disassembly

Cell disassembly should help confirm any deductions made during physical and electrical examination. In silver-zinc cells, the morphology and distribution of the active materials is important and receives emphasis in this procedure. However, other forms of analysis using other than visual or metallographic techniques may be used, as explained in more detail for the nickel-cadmium procedure.

Recharge (Step 2.9) is performed to permit better visual observation of the active materials. Observations should be made immediately after opening the cell because the moist zinc electrodes react exothermally with the oxygen in the air and become hot.

12 SUMMARY

Specifications for accelerated life tests for electrochemical cells have been given. The life tests are designed to operate cells at higher-than-normal gradients (thermal, mechanical, chemical, and electrical stresses) of temperature, pressure, concentration, and voltage. The four stresses provide the basis for a test program and are assumed to accelerate the degradation of electrical quality of a rechargeable battery.

The electrical qualities of a cell are quantitatively measured in units of reciprocal ohms per unit mass. The initial quality Q_0 is to be measured after an acceptance test. At later times, this quality and the quality at a time in use $Q(t)$ are normalized as a ratio $Q(t)/Q_0$ to give dimensionless numbers expected to lie in the interval between 0 and 1. In the accelerated life test, qualities are to be measured at the end of selected charge and discharge regimes. The electrical quality Q_E of a cell is identified as

$$Q_E = \frac{1}{\Delta E n g'},$$

where ΔE denotes an incremental change in cell voltage between the beginning and end of charge or between the beginning and end of discharge, n denotes the hourly rate of charge or discharge, and g' denotes the grams per ampere-hour of cell capacity. Both n and g' are based on the manufacturer's rating of ampere-hour capacity.

It is expected that both the charge and discharge electrical qualities of a cell will gradually decrease over time. Moreover, the higher the interval stresses, the greater will be the time rate of decrease of the electrical qualities. These two assumptions regarding the quality of a cell underlie the structure of the test program wherein relatively short-time changes of quality at a high stress are used to predict the relatively long life under the stress conditions of intended-use operation.

The general test plan consists of operating nominally identical electrochemical cells of a specified type, size, and manufacturer over a range of operating conditions. The number of operating conditions depends on the state of knowledge that exists with respect to the following question: Which of the following environmental and operating conditions contribute to one or more of

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the stated stresses that will jointly affect the time rates of change of quality in a quantitatively known or unknown manner?

(1) Environmental temperature
(2) Rate of change of environmental temperature
(3) Depth of discharge
(4) Rate of discharge
(5) Amount of charging
(6) Rate of charging
(7) Internal gas pressure or external retaining pressure
(8) Rate of generation or decrease of internal or external pressure
(9) Amplitude and frequency of vibration
(10) Electromagnetic radiation

One extreme state of knowledge about variables 1 through 10 occurs when the rate of degradation of electrical quality is a known dominant function of only one of the stresses that can be associated with these variables. An opposite extreme occurs when the rate of degradation of quality is an unknown function of all these variables. In the first situation (known function of one stress), only one experiment is required; in the latter situation (no known functions), a complete factorial design may be required to achieve statistically significant results.

Items 1 through 10 are all capable of being independent variables that could be utilized in devising test programs for accelerated life tests of sealed spacecraft cells. These particular items are listed for consideration because stresses are necessary for accelerating the rate of degradation of quality; stresses are proportional to associated strains and rates of strain; and the four kinds of stresses are important for battery aging and can be created by imposing external variations in thermal energy (items 1 and 2), electrical energy (items 3 through 6), mechanical energy (items 7 and 8), kinetic energy (item 9), and electromagnetic energy (item 10). Items 7 through 10 are neglected in the recommended test programs; however, each time a test program is started, mechanical and radiation effects should be considered to determine if they should be included as variables.

As an aid in such decisions, the following steps are recommended:

(1) Assume that all aging processes in sealed cells will involve the physical movement or restructuring of matter (either active or inactive materials).

(2) Recognize that the movement or rearrangement of matter is a tangible manifestation caused by one or more of the four identified (but intangible) stresses, i.e., gradients of temperature, pressure, concentration, and voltage.

(3) Select by experience, deduce from published literature, or make an assumption on the basis of available evidence as to which of the four

stresses dominates the rate at which the movement or rearrangement of matter affects the electrical quality under intended-use conditions.

(4) Select one of the independent variables (items 1 through 10), and identify the maximum value for that variable for which the dominant stress controls the failure mechanism.

When the dominant failure mechanism associated with an intended use can be linked to the single stress that dominates the rate of aging, and when the acceleration factors have a known relationship with the magnitude of that stress or stress level, only one test is necessary for predicting the life of the cell at the normal stress level. This single test will measure the time rate of degradation of electrical quality at the highest possible stress for which the acceleration factor is valid and for which the function of the stress controlling the dominant failure mechanism is known. When these conditions for a single stress are fulfilled, and when the observed degradation of electrical quality exceeds the experimental error by a factor of approximately 2, a single accelerated test will allow cell life to be predicted. For a prediction with a high level of confidence, only a minimum of the useful life will have been spent in testing. This minimum test time will be less than 1 percent of cell life, if the degradation is detected within 1 percent of the extrapolated life. The confidence level for the life of a particular cell should be based on the predicted lifetime as indicated by testing at least five nominally identical cells under the same conditions.

The size of a complete factorial experiment depends on how many of the four stresses are selected; examples are given in Table 22 in Section 7. A reduction in the size of the test program should be obtained through selection of an appropriate subset (fractional factorial) of the possible combinations of stress levels. The selected fraction is to be determined by consultation between a competent statistician experienced in the design of experiments and an electrochemist who knows which combinations of stresses may have calculable or negligible effects. Thus, it is the electrochemist's duty to minimize the number of stresses S by identifying which stresses may be neglected and which of the 10 conditions above are relevant to the dominant stress or stresses. Hopefully, S can be reduced to one.

Moreover, it is the electrochemist's duty to identify any physical limits on selected stress levels. Thus, if the intended-use condition is known, it is always taken as one test level for the selected stresses. If the intended-use condition is not known, the possible range for each selected stress is divided into four equal intervals between extreme levels selected by the electrochemist. The five resulting test points define the five levels of the stress to be included in the experimental design.

When more than one stress is involved with the degradation of electrical quality, the application of this procedure for each selected stress level will give 5^S-combinations of stress levels for a complete factorial design. However, many

of these combinations may represent operating conditions that are known to be physically impossible, to be dangerous, or to result in explosions; such combinations are to be identified and the ranges associated with the stresses so reduced that the resulting combinations represent feasible operating conditions with five stress levels distributed over the reduced range of each stress. When it is deemed necessary to reduce further the size of the test program, the electrochemist should attempt to define the condition of temperature, charge rate, discharge rate, and so forth associated with the maximum stress level for which the failure mechanism is known to remain unchanged. Then, L may be reduced to three stress levels: (1) operating, (2) maximum, and (3) halfway between operating and maximum.

It is emphasized that a stress combination is not to be eliminated from the test on the grounds that no application has ever used such an operating condition. It is specifically recognized that the extreme stress combinations may not represent desirable operating conditions; however, by operating cells over a feasible range of conditions, it is possible by interpolation to predict the performance and life of cells for applications having operating conditions that fall within the limits of the accelerated test conditions. In fact, because extreme operating conditions are likely to represent severe operating conditions, they are useful in accelerating the degradation processes of a cell so that long-range behavior of the cell may be predicted after a relatively short accelerated test.

The statistician can also help decrease the sample size by eliminating certain test combinations where the electrochemist can ensure that interaction of the independent variables is negligible. Any further reduction in sample size increases the hazard of erroneous decisions. Thus, the minimum experimental size depends upon the acceptable risk. The risk depends on experimental error, sample size, and homogeneity of cell population as well as the state of knowledge available to the electrochemist.

The physical approach to accelerated life tests is based on the assumptions that the intended-use conditions for the cells to be tested can be described, that the single stress controlling the dominant failure mechanism under the intended-use conditions can be identified, and that the relationship between acceleration factors and stress levels is an unknown function. The described tests under these assumptions, then, involve the operation of 50 nominally identical cells of a specified type and manufacturer for each intended-use condition. Five distinct accelerated tests are described, each of which utilizes only one independent variable. A capability to carry out these five physical accelerated life tests is recommended because it is believed that these five kinds of tests include substantially all of the known failure mechanisms and because it should be possible to identify which of the four identified stresses is most apt to control the dominant failure mechanism under the intended-use conditions.

When electrical quality falls to a preselected unacceptable level, a cell is defined to be a failed cell. Parametric failures during each test are defined to

occur whenever electrical quality degrades to preselected levels between the initial quality level and the final unacceptable quality level of a failed cell. Predictions of the elapsed times on test at which these parametric failures will occur are to be made for five calculated increments in electrical quality. These predicted times are to be compared with the actual times recorded during the performance of the accelerated test in order to confirm the acceleration factors.

The statistical approach involves the same independent variables and the same number of replicate samples and definitions of stress, quality, parametric failure, and so forth, but it is utilized when the relationships between stress and the independent variables are unknown.

An empirical approach to accelerated life testing is achieved with the statistical response-surface technique when any one variable or combination of variables can be associated with failure. Polynomial coefficients are calculated initially, and their time rate of change is observed for interpolation and extrapolation. Adjunct studies of failure mechanisms by destructive testing are included to provide confirmation that the failure mechanisms were unchanged at the more severe operating levels of the test program. Empirical observations of previously identified indicators for the prediction of battery failure are also recommended. These empirical indicators are obtained by dividing the discharge into five equal time intervals and the charge period into 10 equal time intervals. Then, early failures are predicted (1) from frequent occurrence of 90-mV increments (or greater) during a time interval near the end of charge or discharge, (2) from frequent occurrence of 40- to 50-mV increments on either charge or discharge portions of the cycle, and (3) from frequent occurrence of 0- to 1-mV increments toward the end of charge.

Procedures for tear-down and failure analyses are included so that electrical performance may be correlated with physical and chemical degradation processes. Tear-down tests are to be used initially to determine the starting cell characteristics. Additional tear-down tests on randomly selected cells, at the five times corresponding to the parametric failure times, are to be used to verify that the assumed failure mechanism indeed is occurring as predicted by the physical approach. With this procedure, the recommended examination and tests will provide physical evidence that starting assumptions are either correct or incorrect. Being correct, of course, gives confidence to the test results; but even if the assumed failure mechanism is incorrect, or if stress levels have been chosen improperly or chosen over an inadequate span of values, the recommended tests, involving a minimum of 55 cells for each test, can still provide a valid accelerated life test because the use of five stress levels should allow valid results to be obtained from each experiment involving up to two linear relationships. The use of five cells at each stress level will also allow statistical confidence levels to be calculated. The physical examination from tear-down analyses gives added physical significance to the recommended tests.

The recommended accelerated test program is a blend of empirical (or cryptanalytic), statistical, and physical approaches to accelerated testing. In the

program's design, the physical approach largely serves to define the quality of a cell and to identify generalized stresses and strains. These, in turn, serve to structure the accelerated test in terms of physical concepts. Additional physical measurements throughout the program, and the utilization of empirical and statistical treatments of the data, help to insure valid accelerated life tests that yield a maximum of information with a minimum expenditure of time and effort constrained by the present state of the art. The cryptanalytic methods are enhanced by combining them with the AID program to assess the statistical significance of the indicators obtained. The response surface method of statistical analysis is well suited to blend with the extrapolations of quality obtained from the stress-strain physical models. When the recommended test program has been reduced to practice, the resulting confidence in the methods will allow the tests to be simplified, thereby providing a practical tool for future space engineers to select batteries.

Appendix A EXPERIMENTAL CONDITIONS USED IN LIFE TESTING

Table A1—*Experimental conditions used*

Test Facility	Contract No., Program Duration	Cell Capacity (A-hr)	Cycle[a]
Battelle-Columbus	AF 33(615)-3701, 1966-1969	20	Simulated synchronous and polar orbits
Eagle-Picher	Air Force SSD, Lockheed Missiles, US-AERDL, 1960-1963	36	50/40 min
General Electric	—	—	55/35 min or 1 or 2 discharges per week or 7-3/4-hr charge of total 10-3/4-hr cycle including rest period after discharge
Gulton	(1962)	—	65/35 min
Gulton	(1961)	20	55/35 min
Gulton	1961-1962	—	65/36 min
Inland Testing	AF 33(616)-7529, 1960-1964	12	55/35 min
Inland Testing	AF 33(616)-7529, S/A-1, 1960-1964	12	55/35 min
		20	55/35 min
Inland Testing	AF 33(657)-8450, S/A-1, AF 33(657)-8450, S/A-2, 1962-1964	20	55/35 min
Inland Testing	NAS 5-1048	3.5, 6.0	60/40 min
Martin-Marietta	NAS 5-3027, 1963-1966	6	Variable
QEL	W11, 252B	6	65/35 min
QEL	W11, 252B	3 to 50	55/35 min
QEL	W11, 252B, 1963-1965	3 to 20	55/35 min
QEL	W11, 252B, 1963-1966	3 to 20	55/35 min, 150/30 min
QEL	W11, 252B, 1963-1967	3 to 20	55/35 min, 150/30 min
Royal Aircraft Establishment (England)	1965	3	60/30 min

[a]Charge/discharge time.

in the life testing of nickel-cadmium cells.

Testing Variables		References
Temperature (K (°C))	Depth of Discharge (%)	
298 (25)	40, 80	18, 23
333 (60)	25	70
273, 298, 313 (0, 25, 40)	21	71
273, 298, 313 (0, 25, 40)	10, 25, 50, 75 to 0.9 V	
273, 298, 313 (0, 25, 40)	10, 25, 50, 75 to 0.9 V	
282, 298, 322 (9, 25, 49)	36 at 282 and 322 K (9° and 49° C; 36, 58, 70 at 298 K (25° C)	72
298 (25)	70	73
258, 282, 305, 316 (–15, 9, 32, 43)	36	74
239, 255, 297, 322 (–34, –18, 24, 49)	25, 50, 60, 75	75
239, 255, 297, 322 (–34, –18, 24, 49)	25, 50, 60, 75	76
263, 278, 298, 308 (–10, 5, 25, 35)	25, 50, 75	
263, 278, 298, 308, 323 (–10, 5, 25, 35, 50)	25, 50, 75	77
263, 298, 323 (–10, 25, 50)	10, 25, 40	–
298 (25)	25, 50, 100	29
283, 298, 313 (10, 25, 40)	50, 100 every 5th cycle	78
273, 298, 323/313 (0, 25, 50/40)	15, 25	79
273, 298, 323/313 (0, 25, 50/40)	15, 25 at 273 and 323/313 K (0° and 50°/40° C); 25, 40 at 298 K (25° C)	80
253, 273, 298, 323/ 313 (–20, 0, 25, 50/40)	25, 40 at 253 and 298 K (–20° and 25° C); 15, 25, 40 at 273 K (0° C); 15, 25 at 323/313 K (50°/ 40° C)	81
253, 273, 298, 323/313 (–20, 0, 25, 50/40)	25, 60 at 253 K (–20° C); 15, 25, 60 at 273 K (0° C); 15, 25 at 323/ 313 K (50°/40° C); 25, 40 at 298 K (25° C)	82
263, 273, 293, 313, 323 (–10, 0, 20, 40, 50)	10	83

Table A2—*Experimental conditions used in the life testing of silver-cadmium cells.*

Testing Facility	Contract No., Program Duration	Cell Capacity (A-hr)	Testing Variables			References
			Cycle[a]	Temperature (K (°C))	Depth of Discharge (%)	
Boeing	NAS 5-2155	12	Simulated 300-mile orbit, 65/35 min	263, 293, 313 (–10, 20, 40)	35	84
Gulton	1961	3	65/35 min	263, 293, 313 (–10, 20, 40)	25, 35, 50, 65	73
		6	55/35 min	298 (25)	25, 35, 50, 65	
Gulton	—	—	55/35 min	298 (25)	20	85
				244, 298, 322 (–29, 25, 49)	17, 33	
Inland Testing	Air Force, 1960	15	85/35 min	298 (25)	50	75
			55/35 min	263, 278, 298, 308, 323 (–10, 5, 25, 35, 50)	25, 50, 75	
Inland Testing	AF 33(616)-7529	15	85/35 min	278, 298, 308, 323 (5, 25, 35, 50)	25, 37.5, 50, 75	76
	AF 33(616)-7529, S/A-1, 1960-1964		22.8/1.2 hr	278, 298, 308, 323 (5, 25, 35, 50)	25, 50, 75	
Inland Testing	AF 33(657)-8450	15, 20	85/35 min	278, 298, 308, 323 (5, 25, 35, 50)	25, 37.5, 50, 75	77
	AF 33(657)-8450, S/A-1, -2, 1962-1964		22.8/1.2 hr	278, 298, 308, 323 (5, 25, 35, 50)	25, 50, 75	
QEL	W11, 252B	3 to 300	23/1 hr 71/1 hr	298 (25)	25, 40	79
QEL	W11, 252B, 1963-1965	5, 12	23/1 hr	273, 298, 313 (0, 25, 40)	20, 50	80

			Charge/discharge time[a]	Temperatures (°C)	Depth of discharge (%)	Ref.
QEL	W11, 252B, 1963-1966	3 to 12	60/30 min, 23/1 hr	253, 273, 298, 313 (-20, 0, 25, 40)	25, 60 at 253 K (-20° C); 20, 25, 40, 50, 60 at 273 K (0° C); 16.7, 20, 25, 40 at 298 K (25° C); 20, 50 at 313 K (40° C)	81
QEL	W11, 252B,	3 to 12	1½, 8, and 24 hr cycles	253, 273, 298, 313 (-20, 0, 25, 40)	25 at 252 K (-20° C); 20, 25, 40, 50 at 273 K (0° C); 16.7, 20, 25, 27, 30, 40, at 298 K (25° C); 20, 50 at 313 K (40° C)	82
Various	USAERDL	—	55/35 min, 60/40 min, 65/35 min, 85/35 min, 18/2 hr, 22.8/1.2 hr	244, 261, 298, 322 (-29, -12, 25, 49), 266, 300 (-7, 27), 298 (25), 278, 298, 308, 323 (5, 25, 35, 50), 300 (27), 278, 298, 308 (5, 25, 35)	17, 33, 10, 25, 35, 50, 75, 25, 50, 75, 100, 25, 50, 70	86

[a]Charge/discharge time.

Table A3—Experimental conditions used in the life testing of silver-zinc cells.

Testing Facility	Contract No., Program Duration	Cell Capacity (A-hr)	Testing Variables			References
			Cycle[a]	Temperature (K (°C))	Depth of Discharge (%)	
Douglas Aircraft	—	1, 4	30/30 min	298, 373, 398 (25, 100, 125)	15	87
General Electric	JPL 952121, NAS 7-100 (prime)	7	60/30 min 60/30 min	408, 418 (135, 145) 298 (25)	35	11
General Motors	AF 33(600)-41600	25	85/35 min	272, 297, 311 (-1, 24, 38)	21, 30, 40	88
General Motors	AF 33(600)-41600	37	85/35 min	283, 300, 311 (10, 27, 38)	25	89
General Motors	JPL 950177, NASw 6 (prime)	25	85/35 min	398 (125)	8, 21	90
General Motors	AF 33(600)-41600, 1961	13 to 48	85/35 min	272, 298, 311 (-1, 25, 38)	21, 29, 40.5	91
Inland Testing	(Air Force, 1960-)	25	22.8/1.2 hr	278, 298, 308, 323 (5, 25, 35, 50)	25, 50, 75	75
Inland Testing	AF 33(616)-7529	25	85/35 min	278, 298, 308, 323 (5, 25, 35, 50)	25, 37.5, 50, 75	76
	AF 33(616)-7529, S/A-1, 1960-1964		22.8/1.2 hr	278, 298, 308, 323 (5, 25, 35, 50)	25, 50, 75	
Inland Testing	AF 33(657)-8450	25	85/35 min	278, 298, 308, 323 (5, 25, 35, 50)	25, 37.5, 50, 75	77
	AF 33(657)-8450, S/A-1, -2, 1962-1964		22.8/1.2 hr	278, 298, 308, 323 (5, 25, 35, 50)	25, 50, 75	

QEL	W11, 252B, 1963-1965	12 to 40	150/30 min	298 (25)	40, 42	80
QEL	W11, 252B, 1963-1964	12 to 40	23/1 hr 23/1 hr	298 (25) 298 (25)	40, 42 40, 42	81
QEL	W11, 252B, 1963-1967	12 to 40	150/30 min 23/1 hr	298 (25)	40, 42	82

[a]Charge/discharge time.

Appendix B GLOSSARY OF TERMS

The definitions of the following terms are based on numerous discussions between NASA, U.S. Air Force, and U.S. Navy personnel active in battery technology.

Accelerated life test: a life test in which higher-than-normal stress levels are used to accelerate the degradation of cell electrical quality in order to predict length of life at normal stress levels.

Acceleration factor: the ratio of a rate of degradation of electrical quality at a higher-than-normal stress level to its rate of degradation at a normal stress level.

Acceptance test: a procedure for determining if cells meet preset specifications.

Age: The calendar time elapsed after a manufacturer has sealed the cell.

Aging: Change of a measured electrical quality over calendar time or over a number of cycles.

Amount factors: an amount factor of energy satisfies the principle of conservation of amounts; is proportional to the size of the energy system; and when multiplied by the appropriate intensity factor, gives units of work. These three criteria for amount factors are important for accelerated tests because amount factors are associated with strains and rates of strain. An amount of electricity is measured in coulombs; an amount of heat is measured in calories; an amount of liquid or gas is measured in cubic centimeters; and an amount of chemicals is measured in moles or their equivalent units.

Charge strain: an amount of recharge measured as a percentage of the amount of discharge.

Charge strain rate: a rate of charge, measured in amperes, which is numerically equal to the manufacturer's rated ampere-hour capacity divided by the hours required to put in that capacity.

Conservation of amounts, principle of: when two or more reservoirs of the same form of energy are allowed to interact with one another, the sum of the amount factors remains constant.

Degradation: a decrease in electrical quality.

Degradation rate: the rate at which electrical quality decreases with time, or with number of charge/discharge cycles, when compared at identical charge and discharge strains and rates of strain.

Depth of discharge: ampere-hours removed during discharge measured as a percentage of the manufacturer's rated ampere-hour capacity.

Discharge strain: depth of discharge.

Discharge strain rate: a rate of discharge measured in amperes which is numerically equivalent to the manufacturer's rated ampere-hour capacity divided by the hours required to remove that capacity.

Dominant failure mechanism: a degradation mechanism in competition with other degradation mechanisms which is judged primarily responsible for the failure determinant.

Electrical quality: a description of the performance of a cell in terms of changes in terminal voltages ΔE after a chosen time of charge or discharge at an hourly rate n such that $Q_E = 1/\Delta Eng'$, where g' is the specific mass of the cell as measured by the cell weight in grams divided by the manufacturer's rated ampere-hour capacity for the cell. Quality has units of reciprocal ohms per gram (mho/g). Qualities must be associated with either charge or discharge, and ΔE is always taken as a positive value so that qualities are always positive.

Failure: the inability of a cell to continue to deliver on discharge, or to accept on charge, a preselected quantity of electrical energy under a specified set of user's tolerances. This definition means all failures are electrical failures.

Failure analysis procedure: a procedure used to arrive at the failure determinant.

Failure determinant: the identification of the component associated with failure together with a description of a condition at the identified component which can be reproduced to yield the failure mode.

Failure mechanism: a sequence of physical or chemical processes resulting in an observed failure determinant.

Failure mode: the electrical parameter or combination of parameters (current, voltage, time) which, when out of tolerance, signifies failure.

Flow: a measure of amount factors per unit time.

Flux: a flow of an amount factor perpendicular to a unit area.

Highest intensity, principle of: when two reservoirs of the same form of energy are allowed to interact with one another, energy always flows from the reservoir having the higher intensity factor.

Intensity factor: an intensity factor of energy satisfies the principle of highest intensity; is independent of the size of the energy system; and when multiplied by an appropriate amount factor, gives the units of work. These three criteria are important for accelerated tests because intensity factors are associated with stresses. The intensity of electricity is measured with volts; the intensity of heat is measured with temperature, the intensity of liquid or gas is measured with pressure, and the intensity of chemicals is measured with concentrations or their equivalent units.

Intensity gradient: a localized change in intensity factor with distance in a direction parallel to a flux of amounts.

Life: the calendar time or the number of charge/discharge cycles between the beginning of cell use and its failure.

Memory effect: a temporary loss of discharge capacity which may be restored by cycling a few times to 100 percent depth of discharge.

Parametric failure: an operational cell is said to be a parametric failure when its quality degrades to a preselected level between its initial quality and an unacceptable quality.

Rate of charge (or discharge): the current in amperes at which a cell is charged or discharged and which is arrived at by dividing the manufacturer's rated ampere-hour capacity by the hours required to deliver that capacity.

Real time: a record of the year, day, hour, minute, and second at which an event occurs in a life test.

Simulated life test: a repetitive operation of a cell under a user's normal or simulated conditions of stress to determine cell life.

Strain: a change in an amount factor per unit area associated with a given applied stress. The product of stress and strain has units of work per unit volume.

Strain rate: a flux associated with an intensity gradient. The product of stress times rate of strain has units of power per unit volume.

Stress: an intensity gradient including temperature gradient, pressure gradient, and so forth. A basic hypothesis of accelerated life tests is that stress leads to a condition or set of conditions associated with the rate of degradation of quality over time and, hence, aging of the cell.

Stress level: a quantitative measure of an intensity gradient.

Tear-down procedure: a disassembly procedure used to characterize the physical and chemical properties of a cell.

Appendix C EQUIPMENT REQUIREMENTS

The following list describes the essential equipment required to perform an accelerated life test as outlined in the various recommendations.

CONTROL AND MONITORING OF LIFE TEST

(1) Five environmental chambers to control temperature within a minimum operating range of 213 through 343 K (-60° through +70° C) (The chambers should be large enough to accommodate a minimum of 50 cells.)
(2) Charge power supplies and regulators
(3) Discharge power supplies and regulators
(4) Cell and group voltage alternators, if needed, to match the ranges of the analog to digital converter
(5) Cell and group temperature sensors and reference junctions
(6) Cell pressure transducers
(7) Program timers and contractors
(8) Alarms and memory relays to identify failed cells

DATA ACQUISITION AND ANALYSIS

(1) Digital clock
(2) Scanner with random channel selection
(3) Analog to digital converter
(4) Printer/punch/magnetic tape recording devices
(5) Amplifiers, as necessary, for the various input signals

TEAR-DOWN AND FAILURE ANALYSIS PROCEDURES

(1) Clean laboratory work space with fume hood
(2) Power supplies with voltage limit control
(3) Voltmeters (1000-Ω/V minimum scaler)
(4) Ammeters
(5) Ohmmeters
(6) Coulometers
(7) Internal-resistance measuring device

(8) Autotransformers

(9) Chart recorders

(10) Cell opener

(11) Balances, sensitive to 0.1 g and 0.1 mg

(12) Infrared spectrometer

(13) Mercury/mercury-oxide reference electrodes

(14) Soxhlet extractor fabricated from nickel

(15) Drying oven

(16) Tank hydrogen

(17) Tank nitrogen

(18) Distilled and deionized water supply

(19) Miscellaneous electrical components, hardware, tools, chemicals, glassware, and so forth

Appendix **D** **FLOW DIAGRAMS FOR EXPERIMENTS**

```
                    ┌─────────────────┐
                    │ Identification  │
                    └────────┬────────┘
                             │
                             ▼
                    ┌─────────────────┐
                    │     Initial     │
                    │   examination   │
                    └────────┬────────┘
                             │
                             ▼
                    ┌─────────────────┐
                    │  Cell matching  │
                    └────────┬────────┘
                             │
              ┌──────────────┴──────────────┐
              ▼                             ▼
      ┌───────────────┐             ┌───────────────┐
      │ Thermal stress│             │Electrical stress│
      │     tests     │             │     tests      │
      └───────┬───────┘             └───────┬────────┘
              │        ◄────────────────────┘
       ┌──────┴──────┐
       ▼             ▼
┌─────────────┐  ┌─────────────┐
│  Qualities  │  │ Parametric  │
│             │  │  failure    │
│             │  │ predictions │
└──────┬──────┘  └──────┬──────┘
       │                │
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┌─────────────┐         │
│ Degradation │         │
│rates of     │         │
│ qualities   │         │
└──────┬──────┘         │
       │    ┌───────────┘
       ▼    ▼
┌─────────────┐         │
│ Prediction  │         │
└──────┬──────┘         │
       │                ▼
       ▼         ┌─────────────┐
┌─────────────┐  │  Tear-down  │
│ Operational │  │  analysis   │
│   failure   │  └──────┬──────┘
└──────┬──────┘         │
       ▼                │
┌─────────────┐         │
│   Failure   │         │
│  analysis   │         │
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│ Validation  │
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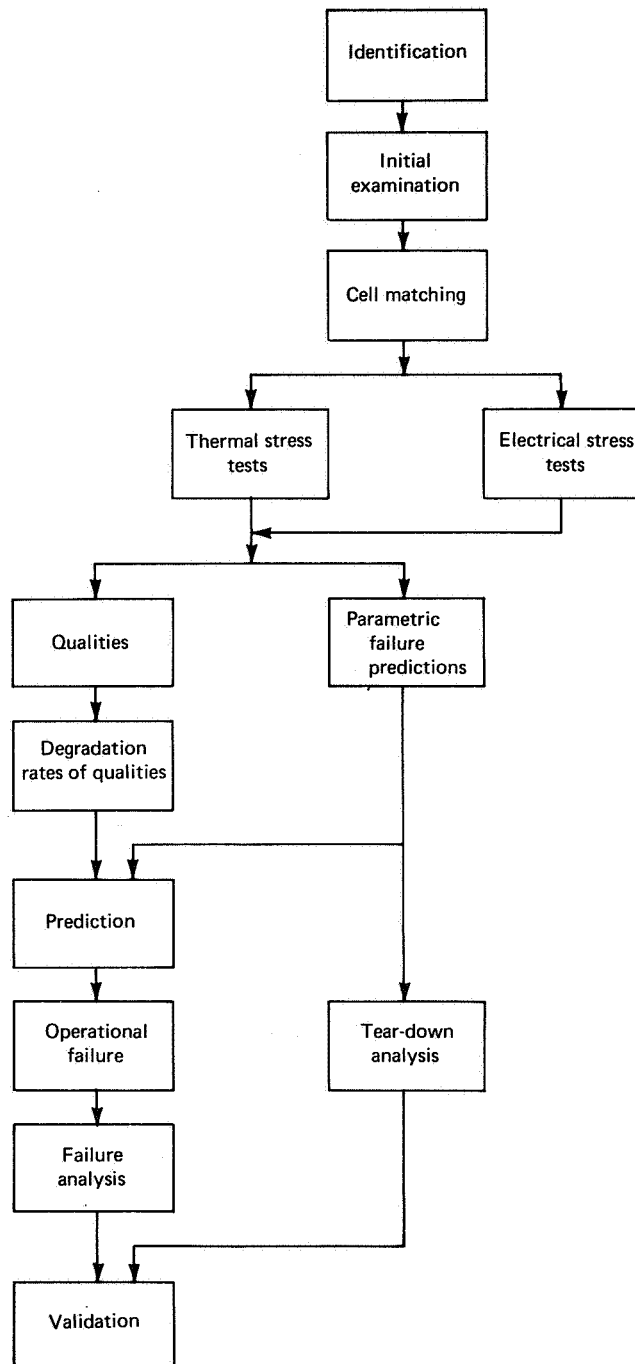
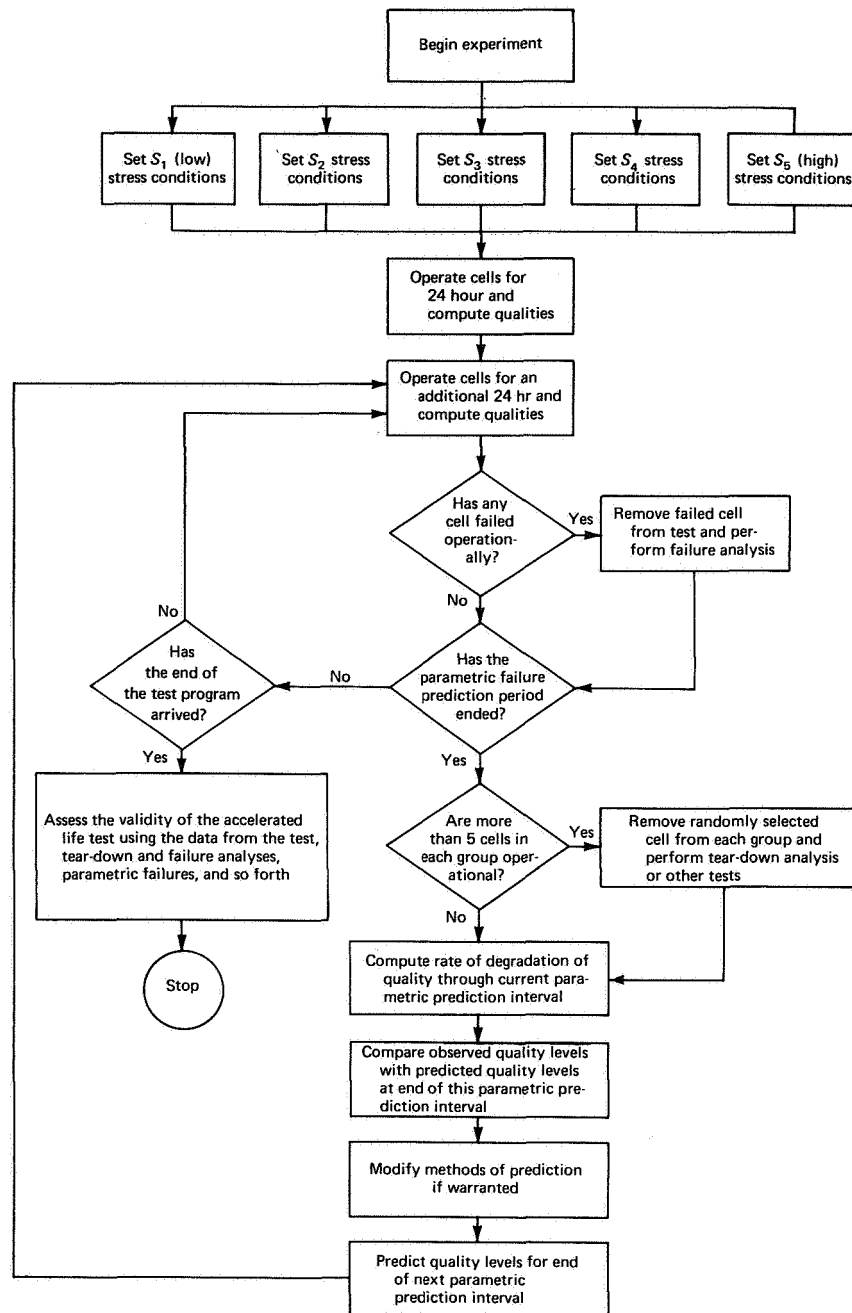Figure D1—Chronology of steps in the recommended accelerated life tests.

Figure D2—Decision flow chart for the performance of the accelerated life test program for each test program.

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(1) Quality, acceptance, and screening tests
(2) Life (operational) tests, including failure analysis tests
(3) Life (accelerated) tests
(4) Test instrumentation and implementation
(5) Data reduction and analysis

A reference is usually given only under the heading in which its main subject matter lies, but when a reference is also believed to contribute useful information to another field it is also listed under that heading.

In addition, the bibliography includes references related to the accelerated testing of components other than batteries. These references are classed as follows:

(1) Life (accelerated) tests for components other than batteries
(2) Mathematical and statistical theories related to accelerated testing

QUALITY, ACCEPTANCE, AND SCREENING TESTS

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